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THERMAL THEORY OF COMBUSTION AND EXPLOSION

III. THEORY OF NORMAL FLAME PROPAGATION

By N. N. Semenov

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THERMAL THEORY OF COMBUSTION AND EXPLOSION

III. THEORY OF NORMAL FLAME PROPAGATION*

By N. N. Semenov

I. EXPERIMENTAL DATA ON FLAME PROPAGATION

On igniting a combustible gas mixture at any point by means of a spark or hot body the process of combustion will be propagated throughout the mass of the mixture. This is what occurs in the explosion of methane in coal mines and of the fuel mixture in the internal combustion engine. If this phenomenon is observed through a glass tube filled with the combustible mixture and ignited by a spark at one end, it will readily be found that along the tube a narrow flame front is propagated, which separates the already burning gas (behind the front) from the fresh as yet un-ignited gas (ahead of the front).

In the above cases the flame moves through an initially stationary gas. In many cases, however, the process of combustion takes place in a combustible gas which is moving toward the ignition source. A stationary flame will then be obtained such as that in the usual Bunsen burner. In each case we are dealing with the same phenomenon of the motion of the flame front with respect to the unburned gas. In the combustion of a homogeneous mixture the combustion proceeds with great intensity because the velocity of the reaction at the flame temperature is very high. The process occurs with much less intensity when the combustible gas is not completely mixed with air, as is the case, for example, in the burning of a naphtha torch flame issuing from a nozzle or in the combustion of a gas burner without air opening. In these cases the rate of combustion is limited not by the speed of reaction but by the rate of the mixing through diffusion of the molecules of the combustible and the oxygen. In Diesel engines and forced furnaces it is attempted to accelerate this process of mixing of the reacting gases by constructional means that will insure the energetic turbulence of the gas. Notwithstanding various mathematical difficulties the theory

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of purely diffusive flames is fundamentally clear since the rate of combustion is determined by simple diffusive processes. Much less understood is the fundamental process of combustion of the combustible gas mixtures which was mentioned earlier. In the present paper we shall concern ourselves precisely with this problem to which our discussion will be limited. We may note, incidentally, in a number of cases the combustible fuel gas is always "mixed". This is the case when the flame is associated with the decomposition of any single given endothermic substance and proceeds without oxygen or air (decomposition of Cl_2O , ozone, vapors of explosive gases, etc.). By the term combustion we shall denote the propagation of the flame in the process of combining with oxygen or during any other chemical processes where a certain amount of energy is liberated and a flame may exist.

The temperature of the gases immediately behind the flame front can be readily computed from the thermodynamic data if the heat losses in the flame zone are not large. This temperature for various compositions of the mixture fluctuates generally between 1500° and 3000°K . Often (on account of dissociation) complete combustion does not take place in the flame front and a part of the substance may complete its combustion behind the flame front. The Bunsen burner generally operates with excess fuel mixtures. The most intense combustion takes place in the inner cone which forms a thin flame cap. In this zone the fuel burns to CO , CO_2 , H_2 , and H_2O , the relative concentration of which is determined by the equilibrium of the hydrogen gas at the combustion temperature. The products CO and H_2 are burned by the diffusion of the oxygen of the air within the wide outer cone of the burner. In this zone the process is determined not by the speed of reaction but by the diffusion.

The two processes in the Bunsen burner may be separated, for which purpose the burner is surrounded by a glass tube held in place by a plug, as shown in figure 1. By this means the cones can be separated. The inner cone (a) as before forms a kind of thin flame cap over the end of the burner. Since the glass tube becomes filled, with the products of combustion intermingled with the products of incomplete combustion and dissociation of the fuel, there is no access of the oxygen of the air to the inside cone and therefore no outer cone of the flame is here formed. At the exit to the air, however, these products can burn by mixing with the oxygen and thus the outer

cone (b) is displaced at the mouth of the tube and the two cones separated.

We shall thus concern ourselves with the process of combustion in homogeneous mixtures taking place in a very thin zone of the flame front. (Later we shall see that the thickness of this zone is of the order of 10^{-2} cm.) This thin zone is sufficient, however, for the reaction processes to take place, the heat given out being expended in heating the fresh cool gas ahead of the flame front to a high temperature. Due to the fact that the gas on one side of the zone consists of the products of reaction and on the other side of the initial substances energetic diffusion processes will take place in this zone. These in sum are the phenomena that occur in the flame front. Our problem is, on the basis of a study of these phenomena, to obtain quantitative expressions for the speed of combustion of the substances in the flame front.

Due to the fact that the zone within which the combustion takes place is very thin, external, artificially produced turbulence and even the motion of the gas arising from the combustion process, will lead only to a curvature of the surface of the flame front and an increase in its area but will not disturb the structure of the zone itself, (They will not, for example, complicate the processes of diffusion and heat transfer in the zone,) Thus any kind of motion or turbulence in the gas only increases the area of the flame front but does not change the characteristics of any element of the front area. Particularly, on a unit area of the flame front of a given mixture the same quantity of fuel per second v_m will always be burned. Therefore the total quantity of fuel burned per second over the entire flame front area S will be $v_m S$. Any curvature of the flame front due to gas flows or turbulence will therefore increase the total quantity of burned fuel in proportion to the increase in the flame front area S . There thus enters in the theory of combustion for each given mixture a certain constant, namely, the mass rate of combustion v_m equal to the number of grams of mixture burned per second per unit area of the flame front.

In burning a definite quantity of fuel per second, the flame front is displaced with respect to the initial gas as fresh quantities of the latter are consumed by the flame. It is not difficult to establish a relation between

the mass rate of combustion and the linear velocity of the displacement of the flame front. In order to secure the combustion of $v_m dS$ grams of the mixture it is necessary that this quantity of the mixture be brought up to the element dS of the flame front either by displacement of the flame front or by having fresh gas supplied to the stationary flame front. For this purpose the linear velocity of displacement of a given element of the flame front with respect to the unburned gas in the direction normal to the flame front surface at a given position should be equal to $v_0 = v_m/\rho_0$ where ρ_0 is the density of the initial cold gas. This linear velocity v_0 is denoted as the "normal velocity of flame propagation."* It is a characteristic constant for the combustion process of every mixture and does not depend on the hydrodynamic conditions under which the combustion occurs.

If the flame front in a tube were plane (or a sphere normal to the axis of the tube) the displacement velocity of the flame front (with ignition at the open end of the tube) would exactly be equal to the normal speed of propagation. Actually the burned gases on expanding flow out through the open end of the tube into the atmosphere according to the law of laminar flow (that is, with velocities varying with the distance from the wall). At the wall itself the flow velocity of the burned gases is equal to zero. It can readily be shown that the burning gases at the flame front edges should flow at an angle to the latter. A detailed though qualitative analysis of the hydrodynamics of the flow of the gases in this case (see Jost reference 1) leads to the conclusion that the plane front is unstable and that the front should assume a curvature. The stable form will be that of a cap which bulges in the direction of motion of the flame. On figure 2 is shown a number of instantaneous flame-front photographs separated by equal time intervals, the front being propagated in a vertical tube ($d = 5$ cm, mixture of 58 percent CO and 42 percent air, pictures by Barsky). For flame propagation in a horizontal tube (if the latter is not too narrow) there will also be a convexity due to gravity which makes the front unsymmetrical with respect to the tube axis (fig. 3). As long as there is no change in the hydrodynamic conditions the shape of the

*Denoted as transformation velocity in NACA reports.
(Translator's note.)

flame front will remain constant, hence also the quantity $v_m S$ of gas burned per second and also the velocity of displacement of the flame front as a whole. This velocity v_{obs} will evidently be equal to $v_m S / \pi r^2 \rho_0$ * where r is the radius of the tube and S as before the total flame-front area, whence $v_{obs} = v_0 S / \pi r^2$, that is, the ratio of the observed velocity of propagation in a certain tube to the normal velocity is as the area of the flame front to that of the tube. Tests show, in fact, that for a distance 0.5 - 1 meter (depending on the total length of the tube) the velocity of propagation of the flame in the tube remains constant. This is seen from figures 2, 3, and 4, which shows a photograph of the flame propagation obtained on a rotating film. (If w is the linear speed of motion of the film $\tan \phi = v_{obs} / w$.) The constancy of the angle ϕ , that is, the rectilinear trace of the flame indicates the constancy of the propagation velocity. By both of these photography methods the value of the observed velocity of propagation can be obtained.

TABLE I

Velocity of flame propagation in 10-percent mixtures of methane with air in tubes of various diameters and computation of the normal velocity of propagation

Diameter of tube (cm)	Direction of flame propagation	Observed velocity of propagation (cm/sec)	Area of flame front (cm ²)	normal velocity (cm/sec)
10	Horizontal	111	300	29
10	----Do----	71	189	29
5	----do----	92	66	27
5	----do----	61.5	48.5	25
2.5	----do----	71.5	12.6	28
2.5	----do----	63	11.0	28
2.5	----do----	59	10.4	28
2.5	vertical up	58	48	28
2.5	same	92.5	66.5	27
2.5	vertical down	61	46	26
2.5	same	58	63.5	26

*For a displacement of the flame front with velocity v_{obs} , the quantity of substance consumed in the flame front per section is $v_{obs} \rho_0 \pi r^2$ grams. On the other hand at the flame front area S there burn each second $v_m S$ grams whence $v_{obs} \rho_0 \pi r^2 = v_m S = v_0 \rho_0 S$.

The first method has the advantage that, besides permitting the computation of the flame-front area S , it also permits the computation by the above formulas of the normal velocity of propagation v_0 . The results of the computation are given in table I.

We see that for tubes of different diameters for various shapes of the flame front and various observed velocities of the flame propagation the computation actually gives a constant (within the limits of observation errors) normal velocity of propagation.*

We have already shown that the uniform flame propagation in a tube is observed only at the start of the process over the first meter of the flame path. Thereafter the flame propagation, for reasons not yet understood, presents a nonuniform character. The flame at times begins to move ahead with a very large velocity; at times the velocity decreases and even reverses its direction - that is, a kind of oscillation begins to take place. This is clearly brought out, for example, in figure 23 (reference 9). It is also seen in figure 3 where the regular flame front, after traveling 50 centimeters along the tube, disappears suddenly and the picture becomes confused owing to the energetic flame oscillations. Sometimes the latter attains a very large amplitude as is seen in figure 5 (reference 9). In many cases there occurs another type of disturbance of the regularity of flame propagation in the tube as shown in figure 6, giving an example of the acceleration of the flame propagation and the occurrence of a detonation wave (taken on a rotating film, stoichiometric mixture of methane, photograph by Sokolik (reference 9)). As may be seen, the flame travels slowly at first with a constant velocity, then the velocity begins to increase gradually and finally at the distance S from the point of ignition the flame propagation enters a new regime characterized by detonation.

*In wide horizontal tubes the convection in the direction of gravity disturbs the correct shape of the flame front, producing in it all kinds of nodes and breaks, a condition which renders impossible the measurement of the normal velocity of propagation. The lower photograph (fig. 12) of the article by Sokolik (reference 9) is an example of this type of flame propagation.

The detonating combustion (like the normal one) progresses at a constant rate with the difference, however, that the detonating velocity exceeds the normal combustion rate hundreds and thousands of times. Detonation does not arise in every mixture but only in mixtures with a sufficiently large amount of heat liberation. The normal propagation is associated with flame propagation through heat conductivity, the flame front heating the neighboring cool layers of fresh gas to a high temperature, insuring a high reaction velocity; whereas in the detonating regime, the flame propagation occurs with the aid of the hydrodynamic shock wave. Over this wave front there is a sudden compression of the unburned gas to a very high pressure. As a result of adiabatic compression the temperature of the gas sharply rises and the mixture reacts suddenly. In our present paper we shall not consider these interesting phenomena which are important both from a theoretical and practical point of view. We shall only touch upon the problems of the fluctuating type of propagation which often arises to disturb the regularity of the normal propagation. There sometimes occur cases where the amplitude of these fluctuations is not large. In these cases, notwithstanding the presence of fluctuations, the average in time of the propagation velocity maintains the same value as the velocity of uniform propagation that occurs at the start of the process. According to Jost this may be considered as proof of the fact that for small fluctuations the flame front remains stable and maintains its shape. Relative to the unburned gas the flame is propagated with the same constant velocity. The reason for the apparent irregularity of motion of the flame with reference to the observer appears to be the oscillation of the gas column in the tube as a whole. These oscillations originate from certain unexplained hydrodynamic causes connected with the motions of the gases during the flame propagation. Small flame oscillations can be made out on figure 2 (successive flame fronts compressed, then rarified).

In those cases where the amplitude of the oscillation becomes large this oscillatory motion of the gas, by changing the distribution of the flow velocity over the tube cross section, leads in turn to a curvature of the flame front, increasing its area and thus also the mean rate of combustion.

Flame acceleration preceding detonation, as Shelkin has shown, also appears as a result of the progressive

increase in area of the flame front and is not associated with any increase in the normal velocity. He showed that this acceleration is observed in the case where the gas motions, arising from the combustion, have a velocity exceeding the critical Reynolds velocity, that is, where turbulence may arise leading to an increase in the area of the combustion front and hence to an increase in the observed velocity of propagation. If the latter is so small that the critical velocity of the gas flow is not reached no detonation arises. If the normal velocity is sufficiently large nonsimultaneous turbulent motions may arise in a smooth tube and gradually increase. For this reason observe at first constant normal velocity of propagation and only after the flame has traversed a more or less long portion of the tube does acceleration of the flame with detonation arise. The correctness of these views was demonstrated directly by Shelkin by observing the flame propagation in a tube with roughened walls (to obtain which he placed a wire spiral inside the tube). The turbulent motions were then expected to arise considerably earlier and this was actually found to be the case, the detonation being found to arise in the immediate neighborhood of the ignition source at a distance of a few centimeters of flame travel; that is, the distance from the source of ignition to the detonating point was shortened more than ten times as compared with a smooth tube.

We thus see that every kind of disturbance in the observed velocity of propagation of the flame is connected either with fluctuation of the gas column or with an increase in the area of the combustion front due to hydrodynamic causes, (for laminar flows by a change in the shape of the flame front and for turbulent flows by an overlaying of the flame front surface by sort of small ripples). The normal velocity of propagation remains, however, constant for all these regimes and detonation appears principally by the new type of the flame propagation.

There are, however, more direct methods of determining the velocity of flame propagation under conditions where the hydrodynamic state of motion of the gas is considerably simpler than for flame propagation along a tube. In the case of flame propagation in a spherical vessel with ignition at the center the entire arrangement

is symmetrical so that only radial flows are possible and there is no reason for the spherical curvature of the flame front.

Radial flow arises from the condition that the gas burning at the flame front (thus enclosed within the flame sphere) has a combustion temperature many times exceeding the temperature of the unburned gas and hence occupies a large volume. This forms a radial flow of unburned gas ahead of the flame front, the velocity of which, compounded with the normal propagation velocity (relative to the unburned gas) leads to an observed velocity v_{obs} considerably in excess of v_0 . In the case where, for the spherical vessel a soap bubble is employed which expands with expansion of the gas, the process of combustion can be carried out at constant pressure and the computation of the observed velocity v_{obs} as a function of the normal velocity v_0 considerably simplified.

Assuming, provisionally, an element of the flame front of unit area as stationary, we know that $v_m = v_0 \rho_0$ grams of unburned gas per second flows up to it, hence the same amount of burned gas is removed. If the density of the burned gas at the temperature of combustion is ρ , the velocity of the burned gas v multiplied by ρ should, according to the law of conservation of matter, be equal to $v_m = v_0 \rho_0$, whence $v_0 \rho_0 = v \rho$ or $v = v_0 \rho_0 / \rho$, $v_0 = v \rho / \rho_0$. But the velocity v with which the burned gas moves relative to the flame front is equal to the velocity of the flame front relative to the burned gas, and since the burned gas under the test conditions is stationary relative to the observer, $v = v_{obs}$ is the observed flame propagation velocity. It may be measured by the two above-mentioned photographic methods, namely:

- (1) by a series of successive instantaneous pictures;
- (2) by photographing the flame motion (expansion of the flame sphere) on a rotating film. (See fig. 16 of the above-mentioned article by Sokolik (reference 9) in which the soap bubble at the beginning and end of the process is indicated schematically).

Thus, knowing v_{obs} , we obtain the normal velocity

$$v_0 = \frac{v_{\text{obs}} \rho}{\rho_0} = v_{\text{obs}} \frac{T_0}{T_1} = v_{\text{obs}} \frac{r_0^3}{r_1^3}$$

where T_0 is the initial temperature of the gas and T_1 the combustion temperature, that is, the temperature of the burned gases. Since according to the Gay-Lussac law the volume $v = 4/3 \pi r^3$ (at constant pressure) is directly proportional to the absolute temperature T the ratio T_0/T_1 will be equal to the ratio r_0^3/r_1^3 where r_0 is the initial radius of the bubble and r_1 the radius of the bubble when all the gas in it is burned. (This radius can readily be found from the photograph.)

We thus obtain an elegant and very clear method from the theoretical point of view for the measurement of the normal velocity of propagation. If we operate with closed tubes or solid closed spherical vessels then as a result of the expansion of the gases during combustion, the pressure as the flame travels, will increase. Since the propagation velocity may depend on the pressure and since the hydrodynamic computation is, in this case, complicated, the method of measuring the normal velocity under these conditions is very difficult. By employing long tubes or large spherical vessels, however, and restricting the measurement to the initial phase of the flame propagation (when the rise in pressure is not large) we may successfully apply to the analysis of the results all the considerations and formulas which were obtained by us for tubes open at one end and for a soap bubble.

The simplest method of all for measuring the normal velocity is by means of the Bunsen burner, that is, the method of the stationary flame. Its disadvantage appears to be only the large expenditure of combustible gas. If the flame front in the tube were plane and hence propagated with the normal velocity v_0 we might, by blowing gas with velocity v_0 toward the flame, bring the flame to rest and thus obtain a stationary flame in the gas stream. The position of the flame, however, would not be stable because small fluctuations in the velocity of the stream would throw the flame forward or backward depending on whether the velocity of the stream was smaller or greater than v_0 . If, in the axis of the tube, we place a point ignition source in the form of a hot point or spark it is possible to increase the velocity of the stream considerably above v_0 and maintain a stable flame.

The flame front will then be in the shape of a cone spreading in the direction of the flow, its vertex situated at the point of ignition and its base on the walls of the tube. The greater the velocity of the stream v the more extended is the cone. The cone angle, the angle between the axis (or the velocity of the stream) and the slant side, is such that $v_0 = v \sin \varphi$. It is readily seen that the quantity of the gas supplied by the stream to a unit area of the combustion cone will be equal to $\rho_0 v \sin \varphi = \rho_0 v_0$ and this magnitude should, as we know, be equal to the mass rate of combustion $v_m = v_0 \rho_0$. From this it is clear that the velocity of the stream may be considerably greater than v_0 without causing a break in the flame. If the ignition source is taken to be not a point on the axis but a heated wire ring placed against the walls of the tube it will then be found without difficulty that the shape of the front should again be a cone having its base on the ignition ring. Both cases are sketched on figure 7.

Tests, such as those described above, are much more easily and simply carried out with a Bunsen burner. At the rim of the burner stagnation points of the flow are formed where the velocity of the flow is small and therefore when the burner is lighted these points play the part of the constant ignition source. The gas stream escaping from the burner (the burner usually operated with laminar flow) moves for a considerable distance in the form of a cylindrical column with the same velocity v that prevails within the burner tube. The conditions are thus obtained for the formation of a stationary conical flame front. Knowing the amount of fuel gas supplied and the cross-sectional area of the burner we determine the velocity v and from the cone angle φ find the normal velocity of propagation $v_0 = v \sin \varphi$. It is simpler to measure not the angle φ but the height h of the cone. The angle φ is then obtained from the equation $\tan \varphi = r/h$ (fig. 8).

The simple conical shape is obtained in the case where the velocity of the gas flow is uniform over the entire tube cross section. Actually with laminar flow of the gas along the tube the velocity distribution is parabolic, being a maximum at the center and falling off toward the walls of the tube. It will readily be seen that under these conditions the stationary flame front

will differ somewhat from the simple cone and will assume the cap shape shown in figure 9. This is, in fact, the shape assumed by the inner cone of a Bunsen burner. For this reason the measurement of the normal velocity, according to the previously given formulas from the height of the cone, involves a certain error. The more accurate method is therefore to photograph the cone and determine its area S from the photographs. Knowing the combustion area and the volume of gas per second V supplied to the burner the normal velocity is easily found from the formula $v_0 = V/S$.

In determining the propagation velocity by the Bunsen cone method it is often more convenient to make use of the arrangement with separated cones.

The greatest number of measurements of the normal velocity refers to air and oxygen mixtures of carbon monoxide, hydrogen, methane or technical combustible gases of the type of illuminating gas. Less study has been devoted to the flames of the higher hydrocarbons. The experimental data thus almost exclusively refers to oxidizing reactions with free oxygen which for practical purposes are of most interest. The processes with other two-component systems (for example, combustion of hydrogen with chlorine and organic substances) and also with one-component systems, that is, the cases of flame propagation with exothermic decomposition of the gaseous substances, have received almost no study (except for the case of flame propagation in ozone).

For two-component systems it is of great interest to establish the dependence of the normal velocity of propagation on the percent of combustible gas (CO , H_2 , CH_4) for various ratios of the oxygen to the inert gas. On figures 10, 11, 12, 13 are shown the corresponding curves for the mixtures CO , H_2 and CH_4 . The propagation velocity for CO and H_2 reaches a maximum, not for the stoichiometric ratios of the components but for a marked excess of the combustible. Dilution of the mixture with inert gas lowers the velocity of propagation of the flame, (see figs. 11 and 12), a fact which is to be expected because the maximum temperature of combustion is thereby reduced. The greater the heat capacity of the inert gas the more the combustion temperature is lowered and the more the flame propagation velocity reduced. Thus, if the mixture of methane and air is first diluted with carbon dioxide and then with argon the

flame propagation velocity in the first case is about half that in the second case..

Preliminary heating of the mixture increases the velocity of flame propagation. On figure 14 are shown the results of Passauer for air mixtures of carbon monoxide containing 2.3 percent water vapor. The flame propagation in mixtures of carbon monoxide depends to a surprising extent on the water vapor content. The propagation velocity increases with increase in the percent moisture. This is shown in figure 15 according to the data of Flock and King. An addition of hydrogen and other substances containing hydrogen has the same effect. A mixture of carbon monoxide with air, or even oxygen that is perfectly dry and without hydrogen-containing substances, is altogether unsuitable for the flame propagation, that is, is not a combustion mixture. If certain substances, having a tendency to take up moisture, as for example, CCl_4 , are added to a mixture of moist CO they strongly reduce the velocity of the flame propagation. These substances produce, however, the same action on the propagation velocity of hydrogen flames where the addition of moisture naturally has no effect.

The problem of the variation of the propagation velocity with pressure has experimentally not been clarified, the results of different authors being in sharp contradiction. Moreover, in tests with CO mixtures where the propagation velocity strongly depends on the amount of moisture, different results are naturally obtained depending on whether the tests are conducted at constant partial pressure of the vapor or at constant percent moisture. The latter case is of theoretical interest but in practice the first one is generally used. On analyzing the data of Ubbelohde, Zeldovich came to the conclusion that at constant percent moisture the normal propagation velocity of CO air mixtures does not depend on the pressure of the mixture. In CO oxygen mixtures the propagation velocity increases somewhat with the pressure, approximately, according to the law $v_0 \approx \sqrt[4]{p}$. In mixtures of hydrogen with air, benzol and benzene the propagation velocity apparently does not depend on the pressure. In methane mixtures the velocity drops with the pressure approximately as $1/\sqrt{p}$. All that can be affirmed with this state of experimentation is that

the velocity of the normal flame propagation in oxidizing reactions varies with the pressure according to the law $v_0 \approx p^n$ where n lies between 0 and $-1/2$. The corresponding mass rate of combustion $v_m = v_0 \rho$ increases with the pressure according to the law p^m where m lies between 1 and $+1/2$. Only in oxygen mixtures where the temperature of combustion is very high is there observed a slight increase in the propagation velocity v_0 with the pressure and a corresponding increase in the mass rate of combustion v_m with the pressure to a power somewhat higher than one.

2. ANALYSIS OF THE OLD THEORETICAL VIEWS ON FLAME PROPAGATION

We have seen that the phenomena of slow flame propagation all lead to the property of the flame front; namely, of a definite quantity v_m grams of mixture burned per unit area of surface or, what amounts to the same thing, of being propagated relative to the nonburning gas in a direction normal to its surface with a propagation velocity v_0 cm/sec. The observed motion of the flame is the result of the superposition of all kinds of hydrodynamic motions upon this fundamental motion of the flame front. Thus, the theory of slow flame-front propagation is the theory of processes occurring in a thin combustion layer in the flame front. Since the curvature of the surface of the flame front is always small in comparison with the thickness of the front (that is, the zone of reaction) we may with sufficient accuracy consider that all magnitudes (for example, temperature) within this zone are functions of a single coordinate, the direction of which is perpendicular to the element of front area (one-dimensional problem). Moreover, by associating the origin of coordinates with the flame front, that is, by studying the process in a system of coordinates moving in space with a given element of the flame front we may assume that the distribution within the combustion and heating zone of all magnitudes of interest (for example, the temperature) does not change with time. The problem thus resolves itself to the solution of the one-dimensional stationary case.

For the computations below, the following notation will be used:

- T_0, T, T_1 respectively, the initial temperature of the unburned gas, the variable temperature in the process of combustion at various points of the flame zone, and the maximum combustion temperature without taking heat losses into account. All temperatures are expressed in degrees on the absolute scale.
- θ the difference $T_1 - T$
- a_0, a the number of molecules per unit volume of the combustible in the initial cold mixture and at various points of the combustion zone, respectively, in the case where a decomposition reaction occurs (Cl_2O, O_3 , explosive substance)
- n, n_0 total number of molecules in the initial mixture at temperatures T and T_0 , respectively
- λ coefficient of heat conductivity of the gas. λ increases with the temperature
- λ^* coefficient of the heat conductivity of the products of combustion at temperature T_1
- c_p specific heat of the gas at constant pressure. c_p increases with the temperature. At first we shall assume c_p independent of the temperature and equal to its average value between T_0 and T_1
- c_p^* specific heat of the products of combustion at the temperature T_1
- H, H_0, H_1 heat contents of unit mass of the gas corresponding to temperatures T, T_0, T_1
- ρ_0, ρ density of the gas at temperatures T_0 and T , respectively
- ρ^* density of the products of combustion at temperature T_1

- v_0 normal velocity of flame propagation in centimeters per second, that is, the velocity of motion of the flame front relative to the unburned gas along the normal to the front surface at a given place (or, what amounts to the same thing, the component along the normal to the front of the velocity of motion of the cold gas relative to the flame front)
- v the velocity of the gas relative to the flame within the combustion zone at temperature T
- v_m the mass rate of combustion, that is, the number of grams of the gas mixture burned per 1 cm^2 of the flame front
- D, D_0 the coefficients of diffusion of the gases at temperature T and T_0 , respectively
- M_0 the fraction of the weight of the combustible in the initial mixture or equivalently the number of grams of combustible per gram of the mixture. In the case of two-component systems, for example, for oxidizing reactions M_0 will be the fraction of the fuel that oxidizes in the process of combustion. M_0 is always ≤ 1
- M the fraction of combustible per gram of the mixture at various points of the combustion zone
 $M \leq 1$
- N the Avogadro number = 6×10^{23} molecules
- Q' the heat of reaction of a single molecule of the combustible and in the case of two-component systems, for example, the oxidation of CO to CO_2 , the heat of oxidation of CO referred to one molecule of CO
- Q the heat of combustion of 1 gram-molecule of combustible (the heat of decomposition of 1 gram-molecule Cl_2O , the heat of combustion of 1 gram-molecule of CO etc.)
- L the heat of combustion of 1 gram of the initial mixture (for the combustion of a single or two-component system diluted with an inert gas; L refers to 1 gram of the entire mixture including the inert gas)

w the speed of reaction expressed by the number of reacting molecules of the combustible per unit volume per second. For the reactions of zero, first and second order $w = Se^{-E/RT}$, $w = kae^{-E/RT}$ and $w = ka^2e^{-E/RT}$, respectively

E energy of activation of the reaction

R gas constant

μ molecular weight of the combustible

Z impact coefficient, that is, the number of impacts per unit time per unit volume between two molecules if the unit volume contained just these two molecules

l free path between impacts

u velocity of the heat motion of the molecules

σ effective diameter of the molecules on impact

m mass of a molecule of the mixture

\bar{m} mean mass of a molecule of the mixture

The following simple relations between the above magnitudes will be required for what follows:

$$M_0 \rho_0 = \frac{a_0 \mu}{N}; \quad \frac{\rho}{\rho_0} = \frac{T_0}{T}; \quad L = \frac{M_0 Q}{\mu} = \frac{M_0 Q' \bar{m}}{\mu} = \frac{M_0 Q'}{\bar{m}}$$

$$= \frac{a_0 Q'}{\rho_0} = H_1 - H_0; \quad Q = N Q'$$

For constant specific heat $L = c_p (T_1 - T_0)$

$$\text{For variable specific heat } H = \int_0^T c_p dT; \quad H_0 = \int_0^{T_0} c_p dT; \quad \left. \begin{aligned} H_1 &= \int_0^{T_1} c_p dT; \quad c_p = \frac{\partial H}{\partial T}; \quad D = \frac{1}{3} u; \quad \lambda = \frac{1}{3} l u c_p; \\ Z &= \sqrt{2} \pi \sigma^2 u; \quad l = \frac{1}{\sqrt{2} \pi \sigma^2 n} = \frac{1}{Z n} \end{aligned} \right\} \quad (A)$$

$$Z = \sqrt{2} \pi \sigma^2 u; \quad l = \frac{1}{\sqrt{2} \pi \sigma^2 n} = \frac{1}{Z n}$$

$$\frac{a \bar{m}}{\rho} = M; \quad \frac{a_0 \bar{m}}{\rho_0} = M_0; \quad N m = \mu; \quad n m = \rho$$

Finally we present various possible definitions of the fuel concentration and the temperature in the combustion zone.

1. a the number of molecules of the combustible per unit volume at different points of the combustion zone. This is the concentration we shall mainly use.

2. $\frac{a}{n} = C$ relative molecular concentration, that is, the fraction of the molecules of the combustible in the mixture at various points of the combustion zone. $\frac{a}{n} \times 100$ percent relative concentration.

3. M the weight concentration of the combustible during combustion (if the molecular weights of all the gases composing the mixture and of their products of combustion are approximately equal to each other $M = a/n = C$), $B = M/M_0$ the relative weight concentration of the combustible. If the molecular weights of all the gases in mixture are the same then

$$\frac{M}{M_0} = \frac{a}{n} : \frac{a_0}{n_0} = \frac{C}{C_0}$$

4. T the absolute temperature at various points of the combustion zone.

5. $T - T_0$ rise in temperature above the initial.

6. $T = (T - T_0) / (T_1 - T_0)$ relative rise in temperature above the initial.

In the flame front within the heating and reaction zone the temperature rises from the initial temperature T_0 of the cold gas to the temperature T_1 , the maximum combustion temperature measured in thousands of degrees.

Considering the temperature distribution within the combustion and heating zones it is not difficult to arrive at the following differential equation

$$\frac{d}{dx} \frac{\lambda}{c_p} \frac{dH}{dx} - v_m \frac{dH}{dx} + wQ' = 0 \quad (1)$$

In the case where λ/c_p may be considered a constant magnitude within the temperature range T_0 to T_1 (that is, in an interval of the order of $1500^\circ - 2500^\circ$) the equation may be written in the form

$$\frac{\lambda}{c_p} \frac{d^2 H}{dx^2} - v_m \frac{dH}{dx} + wQ' = 0 \quad (1')$$

Assuming c_p constant within the range T_0 to T_1 we arrive at the equation

$$\frac{d^2 T}{dx^2} - \alpha \frac{dT}{dx} + \frac{wQ'}{\lambda} = 0 \quad (2)$$

where

$$\alpha = \frac{v_m c_p}{\lambda}$$

then we shall derive this equation. When in the gaseous phase heat is evolved and the heat is transferred from some points of space to others then (even in the absence of forced motion and convection under the action of gravitational forces), there must occur a process of transfer of individual elements of the gas as a result of the heat expansion. Thus even in this case, and all the more in the general case, to the heat conductivity must be added heat transfer arising from the gas motion. We shall denote the linear velocity of the latter by V (a vector which varies in direction and magnitude at different points of the space occupied by the gas). In this case the flow of heat per unit time through an area of 1 cm^2 perpendicular to the direction of V will be $\rho H V$ where ρH is the heat content of a unit volume of the gas. Moreover heat will be transferred by the heat conductivity, the amount being, as is known, $\lambda \text{ grad } T$. The total heat will be equal to

$$\vec{Q} = -\lambda \text{ grad } T + \rho H V$$

If the reaction proceeds with velocity w then each second wQ' cal of heat energy are given out per

unit volume. Hence the change in heat content per unit volume per unit time $\partial(\rho H)/\partial t$ will be equal to

$$\frac{\partial(\rho H)}{\partial t} = - \operatorname{div} \vec{\Omega} + wQ' = \operatorname{div} \{ \operatorname{grad} T - \operatorname{div} (\rho H V) + wQ' \}$$

or making use of the equation of the conservation of matter

$$- \frac{\partial \rho}{\partial t} = \operatorname{div} (\rho V)$$

and of the mathematical relations

$$\frac{\partial(\rho H)}{\partial t} = \rho \frac{\partial H}{\partial t} + H \frac{\partial \rho}{\partial t} \text{ and } \operatorname{div} (\rho H V) = H \operatorname{div} (\rho V) + \rho V \operatorname{grad} H$$

we may rewrite the equation of heat distribution in the form

$$\rho \frac{\partial H}{\partial t} = \operatorname{div} \lambda \operatorname{grad} T - \rho V \operatorname{grad} H + wQ'$$

Using the relations $c_p = \partial H / \partial T$ and $c_p \operatorname{grad} T = \operatorname{grad} H^*$

*Strictly speaking this is not so because in the case of chemical reaction where the composition of the mixture varies in time and space the heat content H varies not only with the temperature but with change in M . If c_1 and c_2 are the specific heats at constant pressure of the initial substances and final products, respectively, then

$$H - H_0 = \int_{T_0}^T [c_1 M + (1 - M) c_2] dT \text{ or } \frac{\partial H}{\partial x} = \left(\frac{\partial H}{\partial T} \right)_M \frac{\partial T}{\partial x} + \left(\frac{\partial H}{\partial M} \right)_T \frac{\partial M}{\partial x};$$

$$\left(\frac{\partial H}{\partial T} \right)_M = c_p = M c_1 + (1 - M) c_2; \left(\frac{\partial H}{\partial M} \right)_T = \int_{T_0}^T (c_1 - c_2) dT$$

From what follows we shall see that under the flame conditions

$$- \frac{\partial T}{\partial x} = \frac{T_1 - T_0}{M_0} \frac{\partial M}{\partial x}$$

where T_1 is the maximum temperature developed in combustion, whence (Footnote continued on page 21)

we may write

$$\text{div } \lambda \text{ grad } T = \text{div } \frac{\lambda}{c_p} \text{ grad } H$$

and rewrite the fundamental equation in the form

$$\rho \frac{\partial H}{\partial t} = \text{div } \frac{\lambda}{c_p} \text{ grad } H - \rho V \text{ grad } H + wQ'$$

* (Footnote continued from page 20)

$$\left(\frac{\partial H}{\partial M} \right)_T \frac{\partial M}{\partial x} : \left(\frac{\partial H}{\partial T} \right)_M \frac{\partial T}{\partial x} =$$

$$- \frac{M_0 \int_{T_0}^T (c_1 - c_2) dT}{(T_1 - T_0) c_p} = \frac{M_0 (\bar{c}_2 - \bar{c}_1)(T - T_0)}{T_1 - T_0 c_p}$$

where \bar{c}_1 and \bar{c}_2 are the mean values of the specific heats in the temperature range T_0 to T . Chemical transformation, as we shall see below, only proceeds at high temperatures for which the difference $c_2 - c_1$ is always small. It is not difficult to prove from tabulated data that even at temperatures of some hundreds of degrees the difference $c_2 - c_1$ for the majority of cases of interest to us is less than 10 percent of the value of c_p . The magnitude $\frac{T - T_0}{T_1 - T_0} M_0$ is always less than unity. We may,

therefore, neglect the term $\frac{\partial H}{\partial M} \frac{\partial M}{\partial x}$ in the expression for

$\frac{\partial H}{\partial x}$ and consider that $\frac{\partial H}{\partial x} = \left(\frac{\partial H}{\partial T} \right)_M \frac{\partial T}{\partial x} = c_p \frac{\partial T}{\partial x}$ or, general-

ized, $c_p \text{ grad } T = \text{grad } H$ as was to be proved. For the same reason the heat Q' or Q given off by the chemical transformation is constant, not depending on the temperature, at which the transformation occurs.

We have, in fact,

$$Q_T = Q_{T_0} + \mu \int_{T_0}^T (c_1 - c_2) dt \approx Q_{T_0}$$

in the case where Q_{T_0} is sufficiently large as is always true in combustion reactions.

or in the one-dimensional case where all the magnitudes depend on a single coordinate x and the velocity vector forms with the x -axis an angle φ (for example, $V \text{ grad } H = V \cos \varphi \frac{\partial H}{\partial x}$)

$$\rho \frac{\partial H}{\partial t} = \frac{\partial}{\partial x} \frac{\lambda}{c_p} \frac{\partial H}{\partial x} - \rho V \cos \varphi \frac{\partial H}{\partial x} + wQ' \quad (2')$$

In applying to the flame zone where as we have seen the problem reduces to the one-dimensional and stationary case ($\partial H / \partial t = 0$) and where $\rho V \cos \varphi$ is no other than the weight of the burning gas mixture per second per unit area of the flame front, that is, $\rho V \cos \varphi = v_m$, we obtain the equation given above.

Previous to the work of Lewis and von Elbe (reference 2) and Zeldovich and Frank-Kamenetsky, partly due to insufficient understanding of the process, partly for the sake of mathematical simplification of the problem, every author introduced into the theory a certain constant, namely, the self-ignition temperature of the given mixture. It was supposed that the fresh gas, on approaching the combustion zone was heated up by the heat given up by the latter to the self-ignition temperature T_i after which the inflammation took place, that is, an intense reaction at a constant rate w was initiated in the mixture until all the substance was consumed and the maximum temperature attained. As we have already seen above (see sec. 1) the self-ignition temperature is not a constant but depends on the test conditions, chiefly on the conditions under which heat is liberated and on the induction period of the zone of inflammation. Moreover, the assumption of a constant speed of reaction on increasing the temperature from T_i to T_1 likewise does not bear criticism. For this reason the introduction of the concept of self-ignition temperature in the problem of the velocity of flame propagation is very reminiscent of the views with regard to the "reaction point" in the self-ignition theory prevalent before van't Hoff.

We shall try, holding to the premises of the previous authors, to present these old theories in their strictest and most logical form without following, in too much detail, the often confused and not always correct concepts which they employed. We stop to consider these old theories based on doubtful premises not only because, until now,

they have been used by scientists and technicians, but also because their clarification will be of value in presenting, in the next section, the new more rigorous thermal theory of flame propagation, the principles of which are explained in the paper by Zeldovich and Frank-Kamenetsky (reference 3). For the solution of the problem we shall make use of equation (2).

Starting from the above naive assumptions we are to formulate the boundary conditions under which equation (2) is to be integrated. We shall lay off the temperature of the gas on the coordinate axis and on the axis of abscissas the distance x from that point in the zone at which the inflammation temperature T_i is attained (fig. 16). The x -axis is directed from the cold initial gas to the products of combustion. In our assumed system of coordinates moving with the flame front the latter is stationary and the fresh gas moves along the x -axis with the velocity v_0 toward the flame front. At $x = -\infty$ the cold gas has the initial temperature T_0 . Then in the heating zone and moving in the direction of positive x the gas is heated by conduction up to the temperature T_i (region I). The gas then starts to react and continues to be heated up (region II). After traversing the distance d from the origin of coordinates the weight of the initial gas has completed its reaction and the temperature attains the maximum combustion temperature T_1 which in the absence of heat losses remains constant further along (region III).

As we have already shown, the reaction velocity w at the self-ignition temperature and above has tacitly or explicitly been assumed constant by the previous authors. It is immaterial whether to assume as constant the number of transformed molecules w per unit volume per unit time independent of the gas density which varies as the gas is heated or the time taken to transform each given molecule, that is, to consider $w/\rho = \text{constant}$ or w proportional to ρ (which changes with the heating). The second assumption leads in the final expression for the propagation velocity to a value less than the first in the ratio 1: $\sqrt{T_0/T_1}$, that is, approximately

$$1: \sqrt{\frac{1}{6}} = \sqrt{6} \approx 2.5$$

The first assumption is equivalent to a reaction of zero order, the second to one of first order with respect to the density or pressure. As we shall see below, for a reaction

of the first order it is necessary to take into account the diffusion in the zone as was not done in the older theories. Only for this reason, in fact, is the assumption of zero order of the reaction in the older theories devoid of inner contradictions and we shall, therefore, stop to consider it.

Let us consider the motion of a small element of volume dw_0 of the initial cold gas at temperature T_0 containing $a_0 dw_0$ molecules of combustible capable of chemical transformation. This element of volume gradually heats up as it moves from $x = -\infty$ in the direction of positive x the volume of the element increasing due to heat expansion so that at a certain distance x and at a corresponding temperature T the volume of the element will be

$$dw = \frac{T}{T_0} dw_0$$

For $T > T_1$ a chemical reaction in the element of volume dw will take place with velocity $w dw$, where w by assumption is a constant magnitude. In the interval dx between x and $x + dx$ the element of volume remains a certain time dt evidently equal to dx/v where v is the velocity of motion of the volume element at the given point. If the cold gas moves with velocity v_0 then on increasing the temperature the gas due to expansion will move more rapidly, namely, with velocity

$$v = v_0 \frac{T}{T_0}$$

so that $dt = dx/v_0 \times T_0/T$

The number of reacting molecules in the element dx is evidently equal to

$$w dw dt = w dw \frac{dx}{v_0} \frac{T_0}{T_1} = \frac{w}{v_0} dx dw_0$$

that is, in each element dx the same number of molecules will react. Therefore, the total number of reacting molecules in the distance between $x = 0$ and $x = d$ of the volume element will be $wd/v_0 \times dw_0$. But by definition all molecules $a_0 dw_0$ of the combustible in the element of volume at the distance d are reacting, whence

$$\frac{dw}{v_0} = a_0 \quad \text{or} \quad d = \frac{a_0 v_0}{w} \quad (3)$$

We thus obtain the required value of the distance d .

In integrating equation (2) we divide the integrating range into two subintervals. In the first one where the temperature rises from $T = T_0$ to $T = T_i$ and x varies from $-\infty$ to 0 no reaction, according to the assumptions made, occurs and hence $w = 0$. In the second interval in which T increases from $T = T_i$ to $T = T_1$ and x from 0 to $x = d$ the speed of the reaction, by the assumption made, is constant. In the third region from $x = d$ to $+\infty$ and $w = 0$ the temperature is constant and equal to T_1 and therefore the solution is obvious. Thus for region I

$$\frac{d^2T}{dx^2} - \alpha \frac{dT}{dx} = 0 \quad (4)$$

where

$$\text{for } x = -\infty, T = T_0 \text{ and for } x = 0, T = T_i \quad (5)$$

In region II

$$\frac{d^2T}{dx^2} - \alpha \frac{dT}{dx} + \frac{wQ_i}{\lambda} = 0 \quad (4')$$

where

$$\text{for } x = 0, T = T_i \text{ and for } x = d, T = T_1 \quad (5')$$

As may be seen these conditions are quite sufficient for the solution of the problem. Besides these, however, there is another condition, namely, the condition of continuity of the heat flow $q = -\lambda \frac{dT}{dx}$ where the two regions meet, that is, the condition

$$\left(\frac{dT}{dx}\right)_{x=0, I} = \left(\frac{dT}{dx}\right)_{x=0, II}$$

This added condition determines the value of the parameter v_o or v_m , that is, the normal velocity of the flame propagation. We find the equation for the determination of v_m or $v_o = v_m/\rho$ to be

$$\frac{T_i - T_o}{T_1 - T_o} = \frac{1 - e^{-\xi}}{\xi} \quad (6)$$

where

$$\xi = \alpha d = \frac{v_m c_p d}{\lambda} = \frac{a_o}{w} \frac{v_o^2 \rho_o c_p}{\lambda} = \frac{v_o^2 \rho_o c_p \tau}{\lambda} \quad (6')$$

and the magnitude a_o/w is denoted by τ .

We shall show how the solution is found. According to formulas (A) and (3)

$$\frac{wQ'}{\lambda} = \frac{wL\mu}{M_o N \lambda} = \frac{v_m c_p (T_1 - T_o)}{d\lambda} = \alpha \frac{T_1 - T_o}{d}$$

Substituting the above in equation (4) and integrating under conditions (5) we find for region I (x from $-\infty$ to 0)

$$(T - T_o)_I = (T_i - T_o)e^{\alpha x} \quad (7)$$

and for region II (x from 0 to d)

$$(T - T_o)_{II} = \frac{T_1 - T_o}{d} x + (T_i - T_o) \frac{e^{\alpha d} - e^{\alpha x}}{e^{\alpha d} - 1} \quad (7')$$

Forming $(dT/dx)_I$ and $(dT/dx)_{II}$ for $x = 0$ and equating them, we obtain

$$\alpha (T_i - T_o) = \frac{T_1 - T_o}{d} - \frac{\alpha (T_i - T_o)}{e^{\alpha d} - 1}$$

whence we obtain formula (6).

When T_i is near T_0 , that is, the self-ignition temperature is low

$$\frac{T_i - T_0}{T_1 - T_0} \ll 1$$

This will be the case when $e^{-\xi}$ is small or ξ is large. Then

$$\frac{T_i - T_0}{T_1 - T_0} = \frac{1}{\xi} = \frac{1}{\alpha d} = \frac{\lambda}{v_0^2 \rho_0 c_p \tau}$$

that is,

$$v_0 = \sqrt{\frac{\lambda}{c_p \rho_0 \tau} \frac{T_1 - T_0}{T_i - T_0}} \quad (8)$$

When T_i is near T_1 , that is, the self-ignition temperature is high, then $(T_i - T_0)/(T_1 - T_0)$ is approximately 1. This will be the case when ξ is small and $e^{-\xi}$ in formula (6) may be developed into a series. Taking the first three terms of the series, we obtain

$$\frac{T_i - T_0}{T_1 - T_0} = \frac{\xi - \frac{\xi^2}{2}}{\xi} = 1 - \frac{\xi}{2} \approx 1 - \frac{\alpha d}{2}$$

(we neglect the term $\xi^2/6 \approx \alpha^2 d^2/6$). Thus

$$\frac{\alpha d}{2} = \frac{T_1 - T_i}{T_1 - T_0}$$

$$v_0 = \sqrt{\frac{2\lambda}{c_p \rho_0 \tau} \frac{T_1 - T_i}{T_1 - T_0}} = \sqrt{\frac{2\lambda}{\rho_0 L a_0} \frac{w}{a_0} (T_1 - T_i)} \quad (9)$$

The formula

$$v_0 = \sqrt{\frac{\lambda}{c_p \rho_0 \tau} \frac{T_1 - T_i}{T_i - T_0}} \quad (10)$$

which is arrived at by most of the previous authors is an approximation, as is readily shown, of the expression of the general formula (6) and, generally speaking, not accurate.

In what follows we shall be especially interested in the case where T_i is near the value T_1 . In this case formula (9) is applicable. We shall estimate the range of application of this formula. We set $\xi = \alpha d = 0.5$. Then neglecting the term $\frac{\xi^2}{6} = \frac{0.25}{6} \approx 0.04$ we make in comparison with $\xi/2 = 0.25$ an error of 16 percent in the determination of the magnitude $T_1 - T_i/T_i - T_0$ or 8 percent in the determination of the velocity v_0 .

Thus the formula is applicable with the required accuracy up to $\frac{T_1 - T_i}{T_i - T_0} \leq 0.25$. If $T_i - T_0 = 2000^\circ$ the formula is applicable up to $T_1 - T_0 = 1500^\circ$ or $T_1 - T_i = 500^\circ$.

In what follows we shall find of importance another approximate method of solution for the case when T_i is near T_1 . This method leads to the same result as formula (9) and hence gives the same degree of accuracy. It differs, however, in this respect, that it may with equal accuracy be applied to cases where the reaction velocity w is not constant but varies, for example, with the temperature. This method was proposed by Zeldovich and Frank-Kamenetsky and is based on the assumption that for T_i near in value to T_1 in equation (4') for region II, it is possible to neglect the second term and write the system in the form:

$$\frac{d^2 T}{dx^2} + \alpha \frac{dT}{dx} = 0 \quad (\text{region I}) \quad (11)$$

$$\frac{d^2 T}{dx^2} + \frac{wQ'}{\lambda} = 0 \quad (\text{region II}) \quad (11')$$

The validity of this will be clear from a consideration of the complete equation (4') if there is substituted in it for the magnitude wQ'/λ its equal $\alpha \frac{T_1 - T_0}{d}$.

Integrating the equation with respect to x from 0 to d we obtain

$$\begin{aligned} -\left(\frac{dT}{dx}\right)_d + \left(\frac{dT}{dx}\right)_0 &= \left(\frac{dT}{dx}\right)_0 = -\int_0^d \alpha \frac{dT}{dx} dx + \frac{\alpha(T_1 - T_0)}{d} \int_0^d dx \\ &= -\alpha(T_1 - T_1) + \alpha(T_1 - T_0) \end{aligned}$$

Since $T_1 - T_1 \ll T_1 - T_0$ the first term on the right side of the equation may be neglected, which means that we may neglect the term $\alpha dT/dx$ in equation (4'), that is, consider the term $\alpha dT/dx$ small by comparison with wQ'/λ and d^2T/dx^2 .*

The physical significance of neglecting the term is the following: In region I the convective heat flow expressed by the term $\alpha(T_1 - T_0)$ is directed toward the positive x values and the flow due to conductivity, expressed by the term dT/dx , is oppositely directed, both flows compensating one another and thus establishing a stationary state. At the boundary of the region the flow of heat by conduction, expressed by the term $(dT/dx)_0$, becomes equal to $\alpha(T_1 - T_0) \approx \alpha(T_1 - T_0)$, that is, practically all the heat in the reaction zone is used in heating the fresh gas. Since the heating in the reaction zone (from temperature $T_1 - T_1$) is very small the heat in region II is conducted away without contributing practically to the further heating of the gas (although the maximum reaction temperature is there attained).

* It may appear strange here why we may consider the magnitude $\alpha dT/dx$ small by comparison with d^2T/dx^2 in region II while in region I these magnitudes are obviously of the same order. This is explained by the fact that on the boundary of the region at point $x=0$ the second derivative undergoes a discontinuity and for $T_1 - T_1 \ll T_1 - T_0$ in region II it is much greater than the second derivative in region I while the first derivatives in both regions are of the same order.

Hence in this region equation (11') is approximately satisfied.

Integrating equation (11) there is obtained

$$\left(\frac{dT}{dx}\right)_0 - \left(\frac{dT}{dx}\right)_{-\infty} = \left(\frac{dT}{dx}\right)_0 = \alpha (T_i - T_0) \equiv \alpha (T_1 - T_0) = \frac{v_0 \rho_0 L}{\lambda}$$

since by assumption T_i is near T_1

Integrating equation (11') there is obtained

$$- \left(\frac{dT}{dx}\right)_d + \left(\frac{dT}{dx}\right)_0 = \left(\frac{dT}{dx}\right)_0 = \sqrt{\frac{2Q'}{\lambda}} \int_{T_i}^{T_1} w \, dT$$

Equating the two expressions obtained for $(dT/dx)_0$, we have the equation for the determination of α or v_0 :

$$\frac{v_0 \rho_0 L}{\lambda} = \sqrt{\frac{2Q'}{\lambda}} \int_{T_i}^{T_1} w \, dT \text{ or } v_0 = \frac{1}{\rho_0 L} \sqrt{2\lambda Q'} \int_{T_i}^{T_1} w \, dT \quad (12)$$

Writing the above in somewhat different form

$$v_0 = \sqrt{\frac{2\lambda Q' a_0}{c_p^2 \rho_0^2} \frac{1}{(T_1 - T_0)^2}}$$

where

$$I = \frac{1}{a_0} \int_{T_0}^{T_1} w \, dT \quad (13)$$

Since

$$a_0 Q' = \frac{a_0 Q}{N} = \rho_0 \frac{Q a_0}{N \rho_0} = \rho_0 \frac{\mu L a_0}{M_0 N \rho_0} = \rho_0 L = \rho_0 c_p (T_1 - T_0)$$

$$v_o = \sqrt{\frac{2\lambda I}{c_p \rho_o (T_1 - T_o)}} = \sqrt{\frac{2\lambda I}{\rho_o L}} \quad (14)$$

Thus expressed the formula is applicable also for w varying with x . If $w = \text{const}$, then $I = \frac{w}{a_o}(T_1 - T_i) = \frac{T_1 - T_i}{\tau}$ and formula (14) leads to formula (9) earlier obtained by another method. It is thus seen that the assumed approximate method of integration has the same accuracy as the expansion of the exact solution (6) in a series to the third term inclusive.

3. NEW THEORY OF FLAME PROPAGATION

In the old theories, as we have seen, two assumptions were made:

1. the mixture starts to react on the attainment of the temperature T_i and
2. the reaction proceeds at a constant speed w .

We know that the reaction speed as a function of the temperature is expressed by the formula.

$$w = S e^{-E/RT}$$

where E is the activation energy, a magnitude characteristic of a given fuel. For substances suitable for combustion this magnitude is usually high and has the value of 25 to 80,000 calories. We should, therefore, expect a very rapid rate of increase in the speed of reaction w with the temperature and, with the coordinate x in the flame. Hence, the assumption of non-dependence of the reaction speed on the temperature in the temperature interval T_i to T_1 is in no way justified. Thus if $E = 60,000$ calories, $T_1 = 2000^\circ$ and $T_i = 1500^\circ$, the speed of reaction increases 120 times in passing from T_i to T_1 . If $E = 30,000$ calories the speed of reaction for the same conditions increases almost 10 times. In the case where $T_1 = 2000^\circ$ and $T_i = 1700^\circ$ the speed in-

creases almost 15 times for $E = 60,000$ and 3 times for $E = 25,000$ calories.

With such a sharp decrease in the reaction speed with decrease in the temperature there is no necessity at all for introducing the self-ignition temperature. As a matter of fact this temperature was needed only for establishing a limit below which no reaction occurs. In actual cases, however, when the reaction speed drops very sharply with lowering in the temperature according to the law $w = Se^{E/RT}$ the latter itself determines the range within which practically no reaction occurs. For this reason we may introduce the notation $T_i = T'$ but no longer as a physical magnitude but as a mathematical device for approximate computation, namely, as that temperature below which there is practically no reaction. It is necessary for us to show that the final result, that is, the computed velocity of propagation will be practically independent of the value chosen for this fictitious magnitude. It is to Zeldovich primarily that we owe this restatement of the problem.*

*Some perplexity is felt by many to be occasioned by the following problem. It is well known that the speed of reaction of most fuels already reaches a very considerable magnitude at temperatures of the order of 1000° . Nevertheless at a flame temperature of 2000° we neglect the reaction speed at 1000° and consider that the entire reaction proceeds only at temperatures near 2000° . The matter is here very simply explained. The velocity of flame propagation, as we have seen, is proportional to the square root of the reaction speed. Hence the greater the latter the greater the flame propagation velocity. For this reason the latter will be fundamentally determined by the maximum possible reaction speed, that is, the speed near the temperature T_1 . The greater this speed the smaller the time interval within which the gas remains in the reaction zone. This interval is so small that in those parts of the zone where the temperature is considerably below T_1 the reaction has no time to proceed at all, although for large time intervals and in closed vessels the reaction speed is sufficiently great at the corresponding temperature. Thus the smallness of the reaction speed in the zone is determined as its smallness with respect to the reaction speed near the maximum combustion temperature.

Under the new assumptions the fundamental equations of heat distribution (1) and (2) remain unchanged except that the speed of reaction w will depend on the temperature according to the law $w = Se^{-E/RT}$ and in the limiting cases instead of T_1 there will enter the above mentioned temperature T' . In the case where the energy of activation E is sufficiently large, namely, when $E/RT_1 \gg 1$ the temperature T' below which the speed of reaction may be neglected will lie near T_1 (which corresponds to the case where $(T_1 - T')/(T_1 - T_0) \ll 1$).

Denoting by θ the difference between T_1 and any temperature T within the reaction zone (between T_1 and T') we may (since $\theta \ll T_1$) set $e^{-E/RT}$ equal to $e^{-E/RT_1} e^{-E\theta/RT_1^2}$. Thus

$$w_1 = Se^{-\frac{E}{RT_1}} e^{-\frac{E\theta}{RT_1^2}} \quad (15)$$

where w_1 is a constant magnitude equal to the reaction speed at the maximum combustion temperature T_1 . We see that the reaction speed drops e times for $\theta = RT_1^2/E$, 7.5 times for $\theta = RT_1^2/E \times 2$, and so forth. For $E = 60,000$ calories and $T_1 = 2000^\circ$ $RT_1^2/E \approx 125^\circ$. Hence for $\theta = 250^\circ$ or $T' = 1750^\circ$ the reaction speed w drops almost 8 times compared with its maximum value w_1 for $T = T_1 = 2000^\circ$. Thus, if we restrict ourselves to this degree of accuracy and neglect the reaction speed at $T < 1750^\circ$ we commit an error not exceeding 12 percent in the determination of v_0 and still less in the determination of v_0 . For such value of θ ($= 250^\circ$) we may: 1) consider $\frac{\theta_1}{T_1} \ll 1$ and make use of the equation (15) and

2) due to the smallness of $T_1 - T'$ by comparison with $T_1 - T_0$ in the solution of the problem make use of the approximate system of equations (11) assuming in them $w = w_1 e^{-E\theta/RT_1^2}$

We then obtain a solution in the form of equation (14) where in the given case

$$I = \int_{T'}^T \frac{w_1}{a_0} e^{-\frac{E\theta}{RT_1^2}} dT = -\frac{w_1}{a_0} \int_{\theta_1}^0 e^{-\frac{E\theta}{RT_1^2}} d\theta = \frac{w_1}{a_0} \frac{RT_1^2}{E} \int_0^{\beta_1} e^{-\beta} d\beta$$

where $\beta_1 = E\theta_1/RT_1^2$

If we choose θ_1 equal to $2RT_1^2/E$, that is, neglect the reaction speed when it is $1/8$ as large as the maximum (w_1) then $\beta = 2$; if we assume $\theta = 3RT_1^2/E$, that is, neglect the reaction speed w when it is $1/2$ as large as w_1 then $\beta = 3$; if $\theta_1 = 4RT_1^2/E$, that is, $w'/w_1 = 50$; then $\beta_1 = 4$.

$$j = \int_0^{\beta_1} e^{-\beta} d\beta = 1 - e^{-\beta_1}$$

If $\beta_1 = 2$, $j = 0.87$; if $\beta_1 = 3$, $j = 0.95$; if $\beta_1 = 4$, $j = 0.98$. Thus we see that the choice of θ_1 provided $\theta_1 \leq 2RT_1^2/E$ has practically no effect on the magnitude j and hence on the speed of reaction. We may thus with an accuracy sufficient for our purposes assume in every case $j = 1$. Otherwise expressed we may everywhere in

formulas (14) and (12) set $\int_{T'}^{T_1} w dT$ equal to $\int_0^{T_1} w dT$.

This very important result permits us to make use of the auxiliary magnitude T' without assigning to it any fundamental significance. In the final result it drops out. Thus

$$I = \frac{w_1}{a_0} \frac{RT_1^2}{E} j = \frac{Se^{-E/RT_1}}{a_0} \frac{RT_1^2}{E}$$

whence according to formula (14)

$$v_0 = \sqrt{\frac{2\lambda}{c_p \rho_0} \frac{Se^{-E/RT_1}}{a_0(T_1 - T_0)} \frac{RT_1^2}{E}} = \sqrt{\frac{2\lambda}{\rho_0} \frac{Se^{-E/RT_1}}{a_0 L} \frac{RT_1^2}{E}} \quad (16)$$

The above equation agrees with formula (9) if the reaction speed w is taken to be $w_1 = Se^{-E/RT_1}$ at the maximum combustion temperature and the difference $T_1 - T_i$ the magnitude RT_1^2/E . In this manner Zeldovich succeeded in ejecting from the formula for the propagation velocity the doubtful constant T_i and the ill-defined magnitude τ , the reaction time.

Even in the above form, however, the theory may not yet be considered satisfactory because the magnitude S

in it was assumed by us to be constant (reaction of zero order). Actually, for all homogeneous reactions S depends in some way on the concentration of the reacting substances. In the case where the combustion represents the reaction of a single substance (decomposition of azomethane, Cl_2O , etc.) the magnitude S is some function of the number of molecules of the combustible in a unit volume of the mixture at a given temperature. In the case of monomolecular reactions $S = ka$, for bimolecular reactions $S = ka^2$. When the initial mixture consists of two reacting kinds of molecules S may be a function of the concentration of both kinds. For bimolecular reactions in this case $S = kab$. The number of molecules a and b are connected with each other by the laws of stoichiometry and diffusion.*

The number of molecules of combustible a in the reaction zone decreases as the reaction progresses. Moreover the reaction products diffuse from the reaction zone into the unburned gas and this also decreases the value of a . The dependence of a on the coordinate x in the flame region may be found from the simultaneous consideration of the equations of diffusion and heat conduction (as was done by Zeldovich and Frank-Kamenetsky) leading to similarity of the temperature and the concentration fields. The same similarity was postulated considerably earlier by Lewis. In the clearest and simplest form this was done by Zeldovich and Frank-Kamenetsky and these authors will be followed in the presentation below. There arises here, however, a very difficult problem with regard to writing down the equations of diffusion and propagation where a temperature gradient exists. Zeldovich writes the expression for the diffusive flow in the usual form $D da/dx$ where D is the coefficient of diffusion of the molecules a into the reaction products. If the special phenomena of thermodiffusion are not taken into account it is evident that for equality of the partial pressure of the molecules a there can be no diffusion flow, whereas in the presence of a temperature gradient the number of molecules in a unit volume will be different at different points.** In this case it

*We exclude, for the present, from consideration the case of two components and take it up below in section 3 in the example of the oxidation of CO .

**Obviously this must be understood as follows. In the field of variable temperature there exists, as usual, the flow $D da/dx$ which, however, is compensated by the reverse mass flow va due to the tendency of the system to balance its pressure. (Footnote continued on p. 36)

is necessary to write the equation of the diffusive flow expressing it through partial pressure.

When the number of molecules does not vary during the reaction (we at first limit ourselves to this case) we may, instead of the partial pressure, make use of the relation between the number of molecules and density of the gas and write the expression for the diffusive flow in the form $D\rho \frac{d(a/\rho)}{dx}$. In this case the change in the number of molecules of the combustible with motion of the gas across the flame front (along the coordinate x) is given by the equation

$$\frac{d}{dx} (D\rho) \frac{d \frac{a}{\rho}}{dx} - v\rho \frac{d \frac{a}{\rho}}{dx} - w = 0 \quad (17)$$

the derivation of which is entirely analogous to that of equation (1).

**(Footnote continued from page 35) Thus if the number of molecules a^* in the equilibrium state is distributed as the gas density, that is, $a^*/\rho = a_0/\rho_0$ or $a^* = a_0\rho/\rho_0$ then the equality of the diffusion and mass flows may be written in the form of the equation

$$D \frac{da^*}{dx} - va^* = 0$$

whence the velocity of the mass flow is

$$v = \frac{D}{a^*} \frac{da^*}{dx} = \frac{D}{\rho} \frac{d\rho}{dx}$$

When the number of molecules a changes in space not in correspondence with the formula $a/\rho = a_0/\rho_0$ we have to deal with true diffusive flow which is composed of the absolute flow $D da/dx$ and the oppositely directed mass flow which balances the pressure and is equal to va where v , as before, is equal to $D/\rho \times d\rho/dx$. Thus the complete diffusive flow is equal to

$$\Omega = -D \frac{da}{dx} + \frac{Da}{\rho} \frac{d\rho}{dx} = -D\rho \frac{d \frac{a}{\rho}}{dx}$$

Since D_p does not depend on the density of the gas and hence to a first approximation also on the temperature (with the same accuracy as λ/c_p) and since $v_p = v_m$ we may write the equation of diffusion of the molecules of combustible in the flame front in the following form:

$$D_p \frac{d^2 \frac{a}{p}}{dx^2} - v_m \frac{d \frac{a}{p}}{dx} - w = 0. \quad (18)$$

The first term expresses the mutual diffusion of the molecules of the combustible and the reaction products under the action of the difference of concentration ahead of and behind the combustion front. The second term expresses the flow of the molecules of the combustible under the action of the gas flow and the third their disappearance due to the reaction.

For $x = -\infty$ $(a/p)_{-\infty} = a_0/p_0$. We introduce a new variable $\alpha = a_0/p_0 - a/p$ and in equation (2) a new variable $\theta = \frac{c_p}{Q'} (T - T_0)$. The two equations then assume the following form:

$$\frac{\lambda}{c_p} \frac{d^2 \theta}{dx^2} - v_m \frac{d \theta}{dx} + w = 0 \quad (19)$$

$$D_p \frac{d^2 \alpha}{dx^2} - v_m \frac{d \alpha}{dx} + w = 0 \quad (19')$$

From the kinetic theory of gases we know that to a first approximation $D_p = \lambda/c_p$. The two equations then become identical.

As we already know the boundary conditions for equation (19) will be

$$(\theta)_{-\infty} = 0; \quad (\theta)_{+\infty} = \frac{c_p}{Q'} (T_1 - T_0) = \frac{L}{Q'} = \frac{M_0 N}{\mu}$$

For equation (18) we have the boundary conditions

$$\left(\frac{a}{\rho}\right)_{-\infty} = \frac{a_0}{\rho_0}, \text{ i. e. } (\alpha)_{-\infty} = 0 \text{ and } (\alpha)_{+\infty} = \frac{a_0}{\rho_0}$$

But according to formula (A)

$$\frac{a_0 \mu}{N M_0 \rho_0} = 1 \text{ or } \frac{a_0}{\rho_0} = \frac{M_0 N}{\mu}$$

that is,

$$(\theta)_{-\infty} = (\alpha)_{-\infty} = 0; \quad (\theta)_{+\infty} = (\alpha)_{+\infty} = \frac{a_0}{\rho_0} = \frac{M_0 N}{\mu}$$

If the equation and the boundary conditions for θ and α coincide, that is, $\alpha = \theta$ in the entire interval

$$\frac{a_0}{\rho_0} - \frac{a}{\rho} = \frac{c_p T}{Q'} - \frac{c_p T_0}{Q'}$$

or

$$c_p T + \frac{\alpha Q'}{\rho} = c_p T_0 + \frac{a_0 Q'}{\rho_0} = c_p T_1 \quad (20)$$

$H = c_p T$ is the store of thermal energy of a unit mass of the mixture.

Since a is the number of molecules of combustible in a unit volume and Q' the energy liberated in a chemical reaction of a single molecule of the combustible, aQ' is the store of potential chemical energy of a unit volume of the mixture and aQ'/ρ is the amount of chemical energy of a unit mass of the mixture. Hence, equation (20) may be formulated thus: The sum of the thermal and chemical energies of a unit mass of the mixture during the combustion process remains constant. That this sum is the same before and after the combustion process seems obvious since it appears to be a simple consequence of the law of

conservation of energy. Since, however, we here have to deal with the phenomena of thermal conductivity and diffusion equation (20), referring to different stages of the combustion process, in no wise appears a consequence of the law of conservation of energy. Thus, if, (as is actually the case), the relation $D_p = c_p/\lambda$ between the coefficients of thermal conductivity and diffusion were not observed it would be easy to show that equation (20) would not be correct. The sum of the energies at some points of the combustion zone would be greater than $c_p T_0 + a_0 Q'/\rho_0$ and at others less. For this reason the demonstration of equation (20) given by Zeldovich and Frank-Kamenetsky is an essential supplement of the work of Lewis who first postulated it. We shall see below how this law can be generalized to the case where D_p is not equal to λ/c_p .

From relation (20) Lewis did not derive any clear and simple conclusions for the general case of flame propagation. He computed, with the aid of this equation, the flame propagation for the individual and very special case of combustion with the decomposition of ozone. Unfortunately he evidently permitted important errors to enter in his derivation. It was possible for Zeldovich from this equation, together with all previous results, to arrive at general conclusions for the combustion theory which we here present, working them out to a greater accuracy.

According to equation (20)

$$a = \rho \left\{ \frac{a_0}{\rho_0} - \frac{c_p (T - T_0)}{Q'} \right\}$$

and since

$$Q' = \frac{Q}{N} = \frac{L\mu}{M_0 N} = \frac{c_p (T_1 - T_0) \mu}{\delta N} \quad \text{and} \quad \frac{a_0}{\rho_0} = \frac{NM_0}{\mu}$$

hence

$$a = \frac{NM_0 \rho}{\mu} \frac{T_1 - T}{T_1 - T_0} = a_0 \frac{\rho}{\rho_0} \frac{T_1 - T}{T_1 - T_0} = a_0 \frac{T_0}{T} \frac{\theta}{T_1 - T_0} \quad (21)$$

Let us return to formula (20) giving the relation between the concentration of the combustible a and the temperature in the heating and reaction zones, rewriting it in the following form:

$$c_p(T_1 - T) = \frac{aQ'}{\rho}$$

or

$$\begin{aligned} \frac{am}{\rho} = M &= \frac{c_p(T_1 - T)}{\frac{Q'}{m}} = \frac{c_p(T_1 - T)}{\frac{Q}{\mu}} = \frac{c_p(T_1 - T)M_0}{L} = \frac{T_1 - T}{T_1 - T_0} M_0 \\ &= \left(1 - \frac{T - T_0}{T_1 - T_0}\right) M_0 = (1 - T) M_0 \end{aligned}$$

or

$$B = \frac{M}{M_0} = (1 - T)$$

That is, the relative weight concentration of the combustible B at any point x of the combustion zone is equal to the difference between unity and the relative rise in temperature T at this point. Since for $x = -\infty$, $B = 1$ and $T = 0$ and for $x = +\infty$, $B = 0$ and $T = 1$ the curves $B - x$ and $T - x$ are symmetrical as schematically shown in figure 17.

Having thus obtained the relation between the number of fuel molecules and the temperature we may now find the velocity of flame propagation without making the incorrect assumption of the nondependence of the speed of reaction w on a which assumption was made in the derivation of formula (9). This computation was first carried out by Zeldovich and Frank-Kamenetsky.*

*We leave out of account the evidently incorrect computation of Lewis and von Elbe for the particular case of the flame propagation in ozone.

In the case of nonomolecular reactions

$$w = k a e^{-E/RT}$$

Substituting this expression in the integral I of formula (13) making use of (21) there is obtained

$$I = \int_{T_1}^T \frac{k a e^{-E/RT}}{a_0} dT = k e^{-E/RT_1} \int_{T_1}^T \frac{T_0}{T} \frac{\theta}{T_1 - T_0} e^{-E\theta/RT_1^2} dT$$

The magnitude T_0/T may be taken outside the integral sign and placed equal to T_0/T_1 because T_1 is near in value to T . In this case

$$I = \frac{k e^{-E/RT_1}}{T_1 - T_0} \frac{T_0}{T_1} \left(\frac{RT_1^2}{E} \right)^j j$$

where $j = \int_0^{\beta_1} e^{-\beta} \beta d\beta = 1 - e^{-\beta_1}(\beta_1 + 1)$
 Choosing

$$\beta_1 = \frac{2RT_1^2}{E}, \frac{3RT_1^2}{E}, \frac{4RT_1^2}{E}$$

we obtain for β_1 the values 2, 3, 4, and for j the values 0.6, 0.8, 0.9. Thus we do not make any large error in the expression for the velocity in setting $j = 1$. In this case, substituting the value of I in formula (14), we obtain,*

* These formulas differ from those of Zeldovich only in that under the square root there stand the magnitudes T_0/T_1 and $(T_0/T_1)^2$ for monomolecular and bimolecular reactions, respectively. The absence of these multipliers in the formula of Zeldovich is associated with a different manner of writing the equation of diffusion.

$$\begin{aligned}
 v_o &= \sqrt{\frac{2\lambda k}{\rho_o c_p} \frac{T_o}{T_1} \frac{e^{-E/RT_1}}{(T_1 - T_o)^2} \left(\frac{RT_1^2}{E}\right)^2} \\
 &= \sqrt{\frac{2\lambda c_p k}{\rho_o L^2} \frac{T_o}{T_1} \left(\frac{RT_1^2}{E}\right)^2 e^{-E/RT_1}} \text{ cm/sec} \quad (22)
 \end{aligned}$$

The corresponding computation for the bimolecular reaction ($w = ka^2e^{-E/RT}$) gives

$$\begin{aligned}
 v_o &= \sqrt{\frac{4\lambda(ka_o)}{\rho_o c_p} \left(\frac{T_o}{T_1}\right)^2 \frac{e^{-E/RT_1}}{(T_1 - T_o)^3} \left(\frac{RT_1^2}{E}\right)^3} \\
 &= \sqrt{\frac{4\lambda(ka_o)c_p^2}{\rho_o L^3} \left(\frac{T_o}{T_1}\right)^2 \left(\frac{RT_1^2}{E}\right)^3 e^{-E/RT_1}} \quad (23)
 \end{aligned}$$

Since the only magnitudes depending on the pressure at which the test is carried out are a_o and ρ_o (both directly proportional to p) the linear velocity v_o for monomolecular reactions is inversely proportional to \sqrt{p} and for bimolecular reactions does not depend on the pressure.

In the derivation of the above formulas we assumed that the main part of the reaction proceeds in a zone situated near the maximum temperature T_1^* and is limited to the temperature range $\theta = T_1 - T'$. As we have seen

*The manner by which the combustion of all the initial gas supplied at a mass rate v_m is maintained when the combustion proceeds in a mixture 90 percent diluted with the products of combustion and containing only 10-15 percent of initial number of molecules of the fuel may appear strange. As before this gas with low fuel content moves with mass velocity v_m and it may be asked where the remaining 90 percent of the mixture is burned. There is no contradiction here and the explanation is that the remaining 90 percent of the fuel is supplied to the boundary region not by the motion of the gas but by the diffusion of the fuel molecules to the place of reaction. Thus all the fuel burns in the combustion zone but under conditions of strong dilution with the reaction products.

the method of solution is approximately true only for $\theta_1 \leq 0.25 T_1$. Since the number of molecules a decreases with increase in the temperature according to formula (21) the mixture, in the range of θ_1 (from $T_1 - T'$ to T_1) will consist mainly of the reaction products and contain a small percent of the initial regulating substances. In connection with this it is necessary to check to what extent, under these conditions, the assumption will be justified that the most rapid reaction takes place within the zone and to what extent the reaction may be neglected at temperatures less than $T' = T_1 - \theta_1$ while maintaining the condition $\theta_1 \leq 0.25 T_1$.

For a bimolecular reaction the conditions will be least favorable. For this case

$$w = ka^2 e^{-\frac{E}{RT}} \approx A \frac{\theta^2}{T_1^2} e^{-\frac{E}{RT}} = A \left(\frac{\theta}{T_1} \right)^2 e^{-\frac{E}{RT_1} \frac{\theta}{T_1} / \left(1 - \frac{\theta}{T_1} \right)}$$

$$= F \left(\frac{\theta}{T_1} \right)^2 e^{-\frac{E}{RT_1} \frac{\theta}{T_1} / \left(1 - \frac{\theta}{T_1} \right)}$$

where F is a certain constant depending on T_1 and $\theta = T_1 - T$. If the reaction velocity is represented as a function of θ/T_1 the shape of the curve will depend on the value of $\gamma = RT_1/E$. Carrying out the computation for $\gamma = 0.05, 0.1$, and 0.2 we shall find that if the reaction velocity w may be neglected for $\gamma = 0.05$, $\theta/T_1 \geq 0.25$, that is, consider that practically the entire reaction occurs at $\theta/T_1 \leq 0.25$ then this is no longer true for $\gamma = 0.2$. Hence for a bimolecular reaction the application of formula (23) is restricted to the values $RT_1/E = 0.1$ or values of the energy of activation E larger than 40,000 at maximum temperature $T_1 \approx 2000^\circ$. For monomolecular reactions conditions will be more favorable and formula (22) will be applicable to cases of practical interest.

The above approximation, fundamental for the theory, may be analyzed more accurately though in a less clear fashion in the following manner: As we have seen the velocity of flame propagation is determined by the in-

tegral $\int_{T'}^{T_1} w dT = I$. We have already shown that this

integral should depend little on the choice of T' . In other words it should differ little from its limiting

value $\int_0^{T_1} w \, dT$. In order that this be true it is necessary that $w(T')$ should be sufficiently small. We obtain a correct result only if the difference $\theta_1 = T_1 - T'$ thus determined does not exceed $0.25 T_1$.

$$I = \int_{T'}^T w \, dT = A e^{-\frac{E}{RT_1} \left(\frac{RT_1^2}{E} \right)^2} \int_0^{\beta_1} e^{-\frac{\beta}{1-\gamma\beta}} \beta^2 \, d\beta = Fj \quad (24)$$

where

$$\beta = \frac{E\theta}{RT_1^2} \text{ and } \beta_1 = \frac{E\theta_1}{RT_1^2} = \frac{1}{\gamma} \frac{\theta_1}{T_1}$$

Figure 18 shows graphically j as a function of β_1 for $\gamma = 0.05, 0.1$ and 0.2 . The arrows indicate the values of β_1 for which j does not differ by more than 10 - 15 percent of its limiting value. We see that these values of β_1 will be 4, 2.5, and 2 and the corresponding values of $\theta_1/T_1 = \gamma\beta_1$ will be 0.2, 0.25, and 0.4. Thus, here too, we come to the same conclusion as before, namely, that the solution is valid only up to values of $\gamma < 0.1$ since for large values of γ the reaction zone is propagated in the temperature range $\theta_1 > 0.25 T_1$ and the assumption that the main part of the bimolecular reaction occurs in the temperature range near T_1 becomes untrue. We may note, by the way, that the limiting value of the integral $j = 2$ obtained above (see formula (23)) is not correct and is associated with neglecting the term $\gamma\beta$ in comparison with unity in formula (24). The value of this integral depends in fact on the parameter γ and for the values most often encountered in tests the limiting value of the integral is equal to unity. In other words under the square root sign in formula (23) there should stand 2 instead of 4.

In the zone of reaction $x > 0$, as we have seen, $T_1 - T$ is small and of order of magnitude equal to RT_1^2/E . We shall denote the concentration a of the fuel molecules for $x > 0$ by a_{eff} . Then according to formula (21) a_{eff} will be of order of magnitude equal to

$$\begin{aligned}
 a_{\text{eff}} &= a_0 \frac{T_0}{T_1} \frac{\frac{RT_1^2}{E}}{T_1 - T_0} = \frac{a_0 c_p}{L} \left(\frac{RT_1^2}{E} \right) \frac{T_0}{T_1} = \frac{a_0 c_p \mu}{M_0 Q' N} \frac{RT_1^2}{E} \left(\frac{T_0}{T_1} \right) \\
 &= \frac{\rho_0 c_p}{Q'} \frac{RT_1^2}{E} \left(\frac{T_0}{T_1} \right) = \frac{\rho_0 c_p T_0}{Q'} \frac{RT_1}{E} = \frac{\rho c_p}{Q'} \frac{RT_1^2}{E} \quad (25)
 \end{aligned}$$

If we consider that the fuel concentration in the combustion zone is constant and equal to a_{eff} we are justified in the solution of the problem of velocity of flame propagation, in making use of formula (16) derived for reactions of zero order substituting $S = ka_{\text{eff}}$ for monomolecular and ka_{eff}^2 for bimolecular reactions. We then, as may be shown without difficulty, obtain the same result as with the strict treatment expressed by formulas (22) and (23). Formula (16) and the expressions for the effective concentration a_{eff} are thus sufficient for obtaining an expression for the velocity of flame propagation in various kinetic cases. In particular this remains true also for the case where the reaction occurs between two components a and b , for example, according to the law

$$w = k a b e^{-E/RT}$$

If there is a deficiency in the component a and an excess in the component b the concentration b' of the component in the reaction zone may be assumed equal to its concentration in the combustion products (it is computed by the stoichiometric equation from the initial state composition of the mixture) and the concentration a_{eff} may be computed by formula (25). Then substituting

the value $w = k a_{\text{eff}} b' e^{-E/RT_1}$ thus computed in formula (16) we obtain a correct result. It is interesting to note that the actual effective concentration of the fuel molecules in the reaction zone does not depend directly on the initial concentration a_0 but is determined only by the maximum temperature of combustion T_1 . Thus, if the latter is maintained constant for various values of a_0 (by substituting, for example, one inert diluting substance for another with a different density or specific heat or by varying the initial temperature of the mixture) then the actual concentration of the fuel in the combustion zone remains constant.

In view of the above circumstance it would be practically impossible for us to determine the order of the reaction from flame propagation tests at constant pressure (varying a_0 by dilution with an inert gas). Since, however, a_{eff} is proportional to the density of the gas or its pressure we may determine the order of the reaction from tests at various pressures. In the case of the combustion of a bimolecular system consisting of molecules A and B we may establish the order of the reaction only relative to that component which is in excess since only its concentration is entirely determined by the initial concentration and is equal to the difference between the initial concentration and the number of molecules entering into the combustion. Thus, in the example considered below of the oxidation of CO, from a comparison of the test data with the formulas for the propagation velocity we can assert only that the speed of reaction is proportional to the water vapor concentration, does not depend on O_2 in oxygen-rich mixtures and is proportional to the CO concentration in mixtures with excess of the latter. Moreover from the dependence on the pressure it may be considered that the reaction has a second order. If the assumption is made that the kinetic law is the same for mixtures rich in oxygen and rich in CO it follows from these data that the speed of reaction is proportional to the product $(CO)(H_2O)$. If, however, this assumption is not made the following law would satisfy the test data: The reaction speed is proportional to the product of the general pressure by (H_2O) in excess O_2 and $(CO)(H_2O)$ in excess CO.

It should be stated that although the new theory, with the aid of the test results on the velocities of propagation, provides much information on the kinetics of homogeneous reactions at temperatures from which the reaction time is measured in 10^{-4} - 10^{-5} seconds (provided by no other methods); from this peculiar nondependence of the effective concentration on the initial concentration no complete guarantee of the uniqueness of the solution of the problem can always be given.

In the derivation of formulas (22) and (23) we made a number of restricting assumptions not always corresponding to the true conditions of the flame propagation. Our further problem will be to free the theory of these restrictions and to extend the formulas obtained to any real case.

These restricting assumptions were:

- (1) the specific heat was constant

- (2) the ratio λ/c_p , that is, the ratio of the heat conductivity to the specific heat was constant
- (3) the number of molecules did not vary during the reaction
- (4) the coefficients of heat conduction and diffusion were equal

In the case that λ/c_p is constant but λ is variable, it is necessary to employ as the variable not the temperature but the heat content H and therefore the equation of heat distribution in the form (1'). The concentration field a/ρ will be similar to the field of heat content, equation (21) being replaced by the equation

$$a = a_0 \frac{\rho}{\rho_0} \frac{H_1 - H}{H_1 - H_0} \quad (26)$$

The method of solving the equation will be entirely analogous to that which was earlier employed except that H will everywhere be substituted for T . Since, however,

in the integral $\int_{H_1}^{H'} w dH$ the temperature enters ex-

plicitly $(w = Se^{-E/RT})$ and H' is the heat content corresponding to a certain temperature T' near T_1 it is necessary to transform this integral to the variable

T in the form $\int_{T_1}^{T'} wc_p dT$ where c_p is variable. More-

over, if the reaction is monomolecular w is proportional to a which is turn in linearly connected with H . There thus enters under the integral c_p^2 and for bimolecular reactions c_p^3 . However, since the temperature interval in which the reaction occurs is not large it may be assumed that within it c_p is constant corresponding to a temperature near the combustion temperature and a composition of the gas approximately that of the products of combustion. We shall denote the value of c_p corresponding to the temperature T_1 by c_p^* and the corresponding value of

the heat conductivity by λ^* . Computation shows that formulas (22) and (23) in their second form hold also for variable specific heat except that for c_p and λ there is substituted c_p^* and λ^* , that is, the specific heat and heat conductivity of the products of reaction at the maximum combustion temperature T_1 .

In the case of non-constant λ/c_p and D_0 we may, in integrating equation (11') assume $\lambda/c_p = \lambda^*/c_p^*$, that is, consider it a constant magnitude because of the smallness of the temperature interval $T_1 - T_0$. With regard to the integration of equation (11) there is substituted $(c_p/\lambda)(T_1 - T_0)$ for $(c_p/\lambda)(T_1 - T_0)$ where (c_p/λ) is defined as

$$\frac{\int_{T_0}^{T_1} \frac{c_p}{\lambda} dT}{T_1 - T_0}$$

Thus in the formula for the flame propagation instead of the magnitude λc_p for the monomolecular and λc_p^2 for the bimolecular reaction there enter correspondingly

$$\left(\frac{\lambda}{c_p}\right)^2 \frac{c_p^*}{\lambda^*} c_p^{*2} \text{ and } \left(\frac{\lambda}{c_p}\right)^2 \frac{c_p^*}{\lambda^*} c_p^{*3}$$

Due to the smallness of these corrections, however, we shall take no further account of them.

If the reaction occurs with change in the number of molecules in the ratio n_1/n_2 then in the reaction zone where the principal mass of the gas consists of the products of reaction the number of fuel molecules will be not

$$\frac{a}{\rho} = \frac{a_0}{\rho_0} \frac{H_1 - H}{H_1 - H_0} \quad \text{but}$$

$$\frac{a}{\rho} = \frac{a_0}{\rho_0} \frac{n_1}{n_2} \frac{H_1 - H}{H_1 - H_0} \quad (27)$$

because the density of the gas varies in the ratio n_1/n_2 . In correspondence with this n_1/n_2 and $(n_1/n_2)^2$ for monomolecular and bimolecular reactions, respectively, enter the formula under the square root sign.

Finally a very important case to consider is the one where $\lambda/c_p \neq D_p$ their ratio being

$$\frac{\lambda}{c_p} : D_p = A : B$$

This is particularly important in the cases of combustion of hydrogen in air or chlorine where the diffusion is determined by the diffusion coefficient of hydrogen and the conductivity by that of the mixture. Simple computation shows that in this case it is necessary to introduce under the square root sign in the formula, the additional factor A/B for monomolecular and $(A/B)^2$ for bimolecular reactions.

In the case $\lambda/c_p : D_p = A : B$ the fundamental equations (19) become

$$A \frac{d^2\theta}{dx^2} - v_m \frac{d\theta}{dx} + w = 0$$

$$B \frac{d^2\alpha}{dx^2} - v_m \frac{d\alpha}{dx} + w = 0$$

According to the law of conservation of energy in the initial and final components

$$(\alpha)_\infty = \alpha_1 = \frac{a_0}{\rho_0} = (\theta)_\infty = \theta_1 = \frac{c_p (T_1 - T_0)}{Q'}$$

$$\text{Since } L = c_p (T_1 - T_0) = a_0 Q' / \rho_0$$

In the reaction zone α and θ , as before, approximately satisfy the equations

$$B \frac{d^2\alpha}{dx^2} + w = 0 \quad A \frac{d^2\theta}{dx^2} + w = 0$$

Integrating in this interval we obtain

$$\left(\frac{d\alpha}{dx}\right)_x - \left(\frac{d\alpha}{dx}\right)_{+\infty} - \frac{d\alpha}{dx} = \frac{1}{B} \int_x^{\infty} w \, dx$$

$$\left(\frac{d\theta}{dx}\right)_x - \left(\frac{d\theta}{dx}\right)_{+\infty} - \frac{d\theta}{dx} = \frac{1}{A} \int_x^{\infty} w \, dx$$

that is,

$$\frac{d\alpha}{dx} = \frac{A}{B} \frac{d\theta}{dx} \text{ and } \alpha = \frac{A}{B} \theta + C$$

Since according to the boundary conditions for $\theta = \theta_1$, $\alpha = \alpha_1 = \theta_1$ we have

$$C = \left(1 - \frac{A}{B}\right) \theta_1$$

whence

$$\alpha = \frac{A}{B} \theta - \left(\frac{A}{B} - 1\right) \theta_1 \quad (28)$$

In region I we may in equations (19) set $w = 0$ whence, integrating once, we obtain

$$A \frac{d\theta}{dx} - v_m \theta = 0$$

$$B \frac{d\alpha}{dx} - v_m \alpha = 0$$

Integrating a second time we obtain

$$\alpha = \alpha' e^{-\frac{v_m x}{B}} \text{ and } \theta = \theta' e^{-\frac{v_m x}{A}}$$

where θ' and α' are the values of θ and α for $x = 0$ bounding regions I and II.

$$\frac{a_0}{\rho_0} - \frac{a}{\rho} = \alpha; \quad \frac{a_0}{\rho_0} = \alpha_1$$

whence

$$\frac{a}{\rho} = \alpha_1 - \alpha = \theta_1 - \alpha$$

or by formula (28)

$$\frac{a}{\rho} = \frac{A}{B} (\theta_1 - \theta)$$

or

$$a = \rho \frac{A}{B} \frac{c_p}{Q'} (T_1 - T) = \frac{A}{B} \frac{\rho}{\rho_0} a_0 \frac{(T_1 - T)}{(T_1 - T_0)} = \frac{A}{B} a_0 \frac{T_0}{T} \frac{T_1 - T}{T_1 - T_0} \quad (29)$$

In other words in the region where the reaction proceeds, the values of a differ from those which would be obtained for $A = B$ (see formula (21)) only by the factor A/B .

In their final form the equations for the normal velocity of propagation, in the case of simple monomolecular or bimolecular reactions with one substance taking part (decomposition of Cl_2O , explosive substances), are written as follows:

$$v_0 = \sqrt{\frac{2\lambda^* c_p^* k}{\rho_0 L^2} \left(\frac{T_0}{T_1}\right) \left(\frac{A}{B}\right) \left(\frac{n_1}{n_2}\right) \left(\frac{RT_1^2}{E}\right)^2 e^{-\frac{E}{RT_1}}} \quad (30)$$

for monomolecular reactions, and

$$v_0 = \sqrt{\frac{2\lambda^* (ka_0)}{\rho_0 L^3} \left(\frac{T_0}{T_1}\right)^2 \left(\frac{A}{B}\right)^2 \left(\frac{n_1}{n_2}\right)^2 \left(\frac{RT_1^2}{E}\right)^3 e^{-\frac{E}{RT_1}}} \quad (31)$$

for bimolecular reactions.

It is necessary to say something about the widths of the heating and reaction zones. In the heating zone (x from $-\infty$ to 0) according to formula (7) for $T_1 - T_0 \approx T_1 - T_0$

$$T - T_0 = (T_1 - T_0) e^{\alpha x}$$

where $\alpha = v_m c_p / \lambda$. This means that the drop in temperature $T - T_0$ from its maximum value $T_1 - T_0$ occurs e times in the distance

$$\xi = \frac{\lambda}{c_p v_m} = \frac{\lambda}{c_p \rho_0} \frac{1}{v_0} \approx \frac{D}{v_0} \frac{c_{pp}^*}{c_p \rho_0} \approx \frac{D}{v_0} \frac{T_0}{T_1} \approx \frac{D_0}{v_0} \frac{T_1}{T_0} \quad (32)$$

where v_0 is the linear velocity of propagation and D_0 the coefficient of diffusion at the initial temperature T_0 . In the majority of cases at atmospheric pressure

$$D_0 \approx 0.2; \quad T_1 \approx 2000^\circ; \quad v_0 \approx 50 \text{ cm/sec}$$

Hence the heating zone

$$\xi = \frac{0.2}{50} \times \frac{2000}{300} = 2.6 \times 10^{-2} \text{ cm} \approx 0.2 - 0.3 \text{ mm}$$

The reaction zone ξ may be roughly estimated as follows from equation (11)

$$\left(\frac{dT}{dx} \right)_0 = \frac{v_m c_p}{\lambda_0} (T_1 - T_0)$$

where $(dT/dx)_0$ is the value of the derivative at the boundary of the reaction zone. We note further that for $x = +\infty$, $(dT/dx)_\infty = 0$. We shall consider that the mean value of dT/dx in the reaction zone will be equal to $\frac{1}{2}(dT/dx)_0$. Hence

$$\frac{dT}{dx} = \frac{1}{2} \frac{v_m c_p}{\lambda} (T_1 - T_0)$$

or, integrating we obtain

$$\xi' \approx 2 \frac{T_1 - T'}{T_1 - T_0} \frac{\lambda}{v_m c_p} \quad (33)$$

As we see, the drop in temperature in the reaction zone is of the order $(T_1 - T') = (T_1 - T_0) 0.2$ whence the reaction zone is of the order of magnitude

$$\xi' \approx 0.4 \xi = 0.4 \times 2.6 \times 10^{-2} \approx 0.1 \text{ mm} = 10^{-2} \text{ cm}$$

The mean free path is of the order 10^{-5} cm at normal temperature and pressure. At 2000° it will be approximately 10 times as large, that is, about 10^{-4} cm. This means that the entire width of the reaction zone is of the order of a hundred times the length of the mean free path. The number of impacts during diffusion in this zone is $n = (\xi/l)^2$, that is, of the order of tens of thousands. The time of stay in the reaction zone is

$$\tau = \frac{\xi'}{v} = \frac{\xi'}{v_0} \frac{T_0}{T_1} = \frac{10^{-2}}{50} \times \frac{3}{20} = 3 \times 10^{-5} \text{ sec}$$

The time between impacts is $1/u \approx 10^{-4}/10^5 = 10^{-9}$, that is, $n \approx 10^4$.

4. CONFIRMATION OF THE THEORY FOR SIMPLE REACTIONS

(THEORY OF COMBUSTION OF EXPLOSIVE SUBSTANCES

AND IN PARTICULAR NITROGLYCOL)

Belayev (reference 4) proposed a theory according to which all easily vaporizable explosive substances burn in the gaseous phase. The surface of the explosive burns continuously by the heat of the combustion conducted to the surface, the heat bringing about vaporization and raising

the temperature at the surface to the boiling temperature T_b and thus supplying a continuous flow of vapor to the combustion zone. For all combustible explosive substances capable of being vaporized without igniting (and which not only detonate but burn) this new point of view regarding their combustion appears to be much more probable than the old conceptions of direct combustion in the condensed phase. Belayev proved his hypothesis by direct test. By photographing the flame of nitroglycol he showed that between meniscus of the liquid and the flame zone there is a narrow dark zone, the width of which is measured in tenths of millimeters at atmospheric pressure and attains 1 millimeter at atmospheric pressure and attains 1 millimeter for combustion at lowered pressure. It is thus possible to consider the theory of Belayev as proven by direct experiment. The mass rate of combustion v_m may be directly measured from the rate of lowering of the meniscus (u) in the combustion of nitroglycol. This directly measured magnitude may be provisionally denoted as the linear velocity of combustion of the liquid nitroglycol. It would be more correct to call it the linear velocity of vaporization in the combustion of nitroglycol. The mass rate of vaporization v_m is evidently equal to the mass rate of combustion of the nitroglycol vapor since all the nitroglycol burns in the form of vapor. The linear speed of combustion of the nitroglycol vapor is therefore

$$v_o = \frac{v_m}{\rho_o} = \frac{[u][\rho]}{\rho_o}$$

where (ρ) is the density of the liquid nitroglycol, ρ_o the density of the nitroglycol vapor at the test pressure and the initial temperature.

Belayev applied the theory of Zeldovich-Frank-Kamenetsky to the computation of the speed of combustion of the nitroglycol vapor. We shall present the computation, making use of the equation of heat propagation, in the form of equation (2).

As was done before we shall divide the entire process into that of region II where the main part of the reaction takes place and where it is possible to neglect the term $v_m c_p dT/dx$ and region I or the preheating region where it is possible to neglect the speed of reaction w . The difference between the present case and that described

above is that region I itself must now be further subdivided into region I' (the dark preheating zone of the vapor) and region I'' of the preheating of the liquid explosive from the initial temperature T_0 to the boiling temperature at the boundary of the liquid and vapor phase (fig. 19). In both regions the same equation applies

$$\lambda \frac{d^2T}{dx^2} + v_m c_p \frac{dT}{dx} = 0$$

except that the constants λ and c_p are different. For the liquid these magnitudes will be denoted (λ) and (c_p) . Since the vaporization associated with the expenditure of thermal energy occurs at the boundary between the liquid and vapor phases of the explosive substance, the flow of heat $\lambda(dt/dx)_b'$ from the vapor side of the boundary surface will be greater than the flow $(\lambda)(dT/dx)_b''$ from the other side of the boundary surface in the liquid phase by the amount of energy required in vaporizing v_m grams of the substance per second per unit area of surface. Hence,

$$v_m F + [\lambda] \left(\frac{dT}{dx} \right)_b'' = \lambda \left(\frac{dT}{dx} \right)_b'$$

where F is the latent heat of vaporization of one gram of the explosive.

The temperature distribution is qualitatively indicated in figure 19. Integrating the equation for region I' we obtain

$$\lambda \left(\frac{dT}{dx} \right)' = v_m c_p (T - T_{\text{boil}}) + \lambda \left(\frac{dT}{dx} \right)_b'$$

Integrating the equation for region I'' we obtain

$$[\lambda] \left(\frac{dT}{dx} \right)_b'' = v_m [c_p] (T_{\text{boil}} - T_0)$$

whence for region I' we obtain

$$\lambda \left(\frac{dT}{dx} \right)' = v_m \left\{ c_p (T - T_{\text{boil}}) + [c_p] (T_{\text{boil}} - T_o) + F \right\} \quad (34)$$

or integrating, the width of the dark preheating zone is obtained as

$$\xi = \frac{\lambda}{v_m c_p} \ln \frac{c_p (T_1 - T_{\text{boil}}) + [c_p] (T_{\text{boil}} - T_o) + F}{[c_p] (T_{\text{boil}} - T_o) + F} \quad (35)$$

The magnitude in the numerator under the logarithm sign is no other than the heat of combustion of 1 gram of the liquid explosive. Thus

$$\xi = \frac{\lambda}{c_p v_m} \ln \frac{L}{[c_p] (T_{\text{boil}} - T_o) + F} \quad (35')$$

As regards flame propagation velocity the latter will be expressed by the same formulas (30) and (31) as for the gas because in zone II the equation is the same as for the gaseous case and the expression for the derivative according to formula (34) is

$$\lambda \left(\frac{dT}{dx} \right)'_o = v_m L$$

A study of the speed of combustion of nitroglycol shows that (u) increases in direct proportion to the external pressure p , that is, $(u) = \rho_o v_o / (\rho)$ where ρ_o is directly proportional to p and the density of the liquid (ρ) does not depend on the pressure. As we have seen, the formula v_o varies in inverse proportion to \sqrt{p} for monomolecular reactions and is independent of p for bimolecular reactions. Thus, in order to satisfy the test data with regard to the dependence of the speed of combustion of liquid nitroglycol on the pressure, we

must assume that the reaction is bimolecular. On the other hand, direct study by Appin of the slow decomposition of nitroglycol vapor at low temperatures and pressures has shown that the speed of reaction obeys the monomolecular law $w = 10^{14} a e^{-\frac{35000}{RT}}$

Belayev assumes that at the high temperatures corresponding to the combustion zone, the speed of activation of the molecules as a result of the impacts becomes insufficient for the establishing of a stationary concentration (computed from statistical data) of the active molecules. The speed of reaction then begins to be determined by the number of activating impacts, that is, becomes bimolecular. A similar phenomenon has long been known for all monomolecular reactions which with the lowering of pressure show a drop of the molecular constant and hence for sufficiently low pressures become bimolecular. It is also known that with increase in the temperature the drop in the constant with decreasing pressure becomes more sharp and thus the pressures at which the reaction passes over into the bimolecular increase.

It is possible that in this way the hypothesis of Belayev should be explained according to which at very high temperatures of the reaction the decomposition of the nitroglycol is bimolecular, even at atmospheric pressure. It should be noted that according to test results on the kinetics of monomolecular decomposition the reaction products as a rule are capable of as good activation of the molecules of the initial substance on impact as the impingement of two molecules of the initial substance. Thus the bimolecularity of these reactions is exceptional. Whereas, for example, for the usual bimolecular reaction of the type $2HJ = H_2 + J_2$, the decomposition is possible only on the impact of two particles of the initial substance and $w = k a^2 e^{-\frac{E}{RT}}$; in this case the activated molecule of the nitroglycol decomposes by itself and the reaction is possible on impact with any particle, particularly with particles of the products of its decomposition, whence

$$w = Z a (M) e^{-\frac{E}{RT}}$$

where (M) is the number of all molecules (both of nitroglycol and of the products of its decomposition) in a unit volume.

The number (M) is determined by the initial number of molecules of nitroglycol a_0 and is equal to $a_0 T_0 / T_1$ whence

$$w = (Za_0) a e^{-E/RT_1} \frac{T_0}{T_1}$$

Remembering the character of the derivation of the expression for the velocity v_0 we shall see that it will be determined not by the expression for bimolecular reactions but by the expression for monomolecular reactions with this difference only, that instead of the constant of first order $k (\sim 10^{13} - 10^{14})$, we shall have

$$Za \approx \sqrt{2\pi} \sigma^2 u a_0 \frac{T_0}{T_1} \approx 10^{10}$$

In the case that $A = B$, we obtain

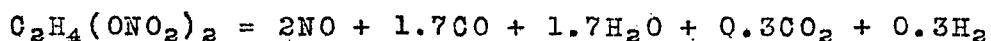
$$v_0 = \sqrt{\frac{2\lambda * Za_0}{\rho_0 L^2} \left(\frac{T_0}{T_1}\right)^2 \left(\frac{n_1}{n_2}\right) \left(\frac{RT_1^2}{E}\right)^2 e^{-\frac{E}{RT_1}}} \quad (36)$$

As in the case of purely bimolecular reactions v_0 does not depend on the pressure p because a_0 and ρ_0 are directly proportional to the pressure. Hence u and v_m will in correspondence with the test be directly proportional to the pressure. Since $\rho_0 = \mu a_0 / N$ where μ is the molecular weight of the nitroglycol,

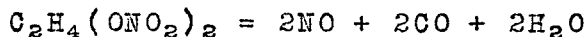
$$v_m = \sqrt{\frac{2\lambda * Za_0^2}{L^2} \frac{\mu}{N} c_p^* \left(\frac{T_0}{T_1}\right)^2 \left(\frac{n_1}{n_2}\right) \left(\frac{RT_1^2}{E}\right)^2 e^{-\frac{E}{RT_1}}} \quad (36')$$

The fundamental magnitude for the computation of the speed of combustion is the heat of decomposition L of the nitroglycol in the flame during its combustion in an inert atmosphere. In the case of its combustion in air there arises, as we have seen, a secondary flame of combustion of the products of the primary decomposition. This secondary process has no relation with the speed of combustion and

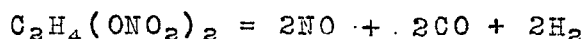
we are therefore interested only in the heat of combustion of the primary process which readily occurs in an inert atmosphere. Direct measurement of L has not been made. Appin, however, determined the products of the primary flame by direct analysis. The latter gave the following final chemical equation for the decomposition:



This shows that the greater part of the molecules is decomposed according to the equation



and a smaller part according to the equation



Computing the heat of this decomposition of nitroglycol on the basis of the heat of formation, as recommended by A. Schmit, Belayev arrives at a value $L = 450$ calories per gram. Knowing L and using the mean specific heat of the reaction products given in the tables of Lewis and von Elbe, Belayev arrives at the following value for the maximum combustion temperature:

$$T_1 - T_0 = 1350^\circ \text{ or } T_1 = 1350^\circ + 300^\circ = 1650^\circ \text{K}$$

The energy of activation E is taken by Belayev from the tests of Appin for low-temperature decomposition of the nitroglycol vapor equal to 35,000 calories. The specific heat of the reaction products for $T_1 = 1650^\circ \text{K}$ is computed by Belayev from the data of Lewis and von Elbe as $c_p^* = 0.35$. The heat conductivity of the products for $T = T_1$ was computed from the mean conductivities at 0°C and then corrected for the temperature 1650°K by the correction of Ceteriand. The ratio of the number of initial to the number of final molecules $n_1/n_2 = 1/6$ (according to the stoichiometric equation).

We shall carry out these computations by a somewhat different method. According to the kinetic theory of gases $\frac{\lambda Z}{\rho_0} = \frac{1}{3} \frac{u^2 c_p}{n_0}$ (for derivation see below, section 5).

In the case of the decomposition of the vapor of pure nitroglycol $n_0 = a_0$

$$u^2 \approx \frac{3 \times 83 \times 10^6 \times T_1}{\mu} \approx \frac{3 \times 83 \times 10^6 \times 1650}{\mu} \approx \frac{4 \times 10^{11}}{\mu}$$

Both as regards the number of impacts and the heat conduction the principal role in the combustion zone will be played by the molecules of the decomposition products of nitroglycol, these being the lighter. Their value of μ must therefore enter the formula. Assuming $\mu = 30$ we have

$$u^2 = \frac{4}{3} \times 10^{10}; \quad c_p = 0.35$$

whence

$$\frac{\lambda Z}{\rho_0} = \frac{1.5 \times 10^9}{a_0}; \quad e^{-\frac{E}{RT_1}} = e^{-\frac{35000}{3300}} = e^{-10.6} = 2.5 \times 10^{-5}$$

$$\left(\frac{T_0}{T_1}\right)^2 = \left(\frac{300}{1650}\right)^2 = \frac{1}{30}; \quad \frac{n_1}{n_2} = \frac{1}{6} \left(\frac{RT^2}{F}\right)^2 = \left(\frac{2 \times 1650^2}{35000}\right)^2 = 2.34 \times 10^4$$

Substituting all these values in formula (36) we obtain

$$v_0 = \sqrt{\frac{2 \times 1.5 \times 10^9}{2 \times 10^5} \frac{2.34 \times 10^4 \times 2.5 \times 10^{-5}}{30 \times 6}} = \sqrt{50} \approx 7 \text{ cm/sec}$$

and the corresponding mass rate of reaction $v_m = v_0 \rho_0$ at $p \approx 7 \times 10^{-3}$ gives $v_m = 4 \times 9 \times 10^{-2} \text{ g/sec cm}^2$. The value actually observed, by Belayev at room temperature is $4 \times 5 \times 10^{-2} \text{ g/sec cm}^2$. The agreement between the theory and experiment is therefore extremely good.

On increasing the initial temperature T_0 at a given heat L the maximum temperature T_1 increases and hence also the velocity of reaction and the velocity of flame propagation. Belayev computed temperatures T_1 corresponding to various values of T_0 from 20° to 200° . Moreover, he experimentally determined the speed of combustion u (proportional to v_m) at various temperatures T_0 . We present below some of the results.

TABLE 2

T_0 in $^\circ\text{C}$	T_1 in $^\circ\text{K}$	T_0 in $^\circ\text{C}$	$u = \frac{v_m}{\rho_0}$
20	1650	20	0.29
50	1685	60	.33
110	1753	100	.44
140	1790	140	.52
170	1828	180	.57
200	1867		

The relation between T_1 and $u = v_m/\rho_0$, as is seen from the formula, is

$$\ln \frac{u}{T_1} = \frac{E}{2RT_1} + C_1 \quad \text{and} \quad \lg \frac{u}{T_1} = \frac{E}{2.34 \times 2 \times 2T_1} + C^*$$

Substituting for each given T_0 the computed T_1 and the experimentally determined u , we should obtain a linear relation between $\lg u/T_1$ and $1/T_1$ with the slope.

$$\frac{E}{9.2} = \frac{35000}{9.2} = 3800$$

Figure 20 shows the experimentally determined relation between $\lg u/T_1$ and $1/T_1$ for liquid nitroglycol (data of Belayev). We see that the points with some scatter

* T_0 does not enter since, according to formula (36) with increase in T_0 , there is a simultaneous decrease in a_0 so that $(a_0 T_0)^2$ remains constant.

arrange themselves on a straight line with a slope equal to 4100.

The above results thus also confirm the theory of flame propagation and give, for the energy of activation, a value practically coinciding with the value 35,000 assumed by us according to the tests of Appin for the computation of the absolute velocities.

In conclusion we shall compare the observed and computed widths of the heating zone. Substituting in formula (35) the value $\lambda^* = 2 \times 10^{-4}$, $c_p^* = 0.4$ and $v_m = 4.5 \times 10^{-2}$ the heat of vaporization of nitroglycol $F = 43,000$ calories and the boiling temperature $T_b = 200^\circ\text{C}$, we obtain $\xi = 0.2$ millimeters. The width of the dark zone at atmospheric pressure directly measured by Belayev (microphotograph and flame photograph) gave a value of the same order of magnitude.

Since the velocity v_m varies in direct proportion with the pressure, with decrease in the latter, the width of the dark zone should increase in inverse proportion to the pressure and, as a matter of fact, the tests of Belayev for pressures of 100 millimeters give a width of the dark zone of the order of 1 millimeter. Thus the tests of Belayev give excellent confirmation of the new theory of flame propagation.

5. CHECK OF THE THEORY BY EXAMPLE OF A CHAIN OXIDIZING REACTION (THEORY OF FLAME PROPAGATION IN CARBON MONOXIDE, AIR, AND CARBON MONOXIDE - OXYGEN MIXTURES)

One of the most important combustion reactions is that of the combustion of carbon monoxide. Together with the oxidation of hydrogen this reaction determines also the combustion of hydrocarbons (since it may be assumed that in the heating zone the hydrocarbons are first transformed into CO and H₂ which then burn).

The oxidizing reaction of hydrogen represents a chain reaction with many branches. (The question as to the application of the theory of Zeldovich to this type of reaction still remains open.) In contrast to this the oxidizing reaction of CO represents a chain reaction, the velocity of which very soon attains stationary values, and we may assume that

notwithstanding the small width of the flame front the velocity of this reaction is completely determined by the temperature and the concentration at any given place within the combustion zone. This behavior of the oxidizing reaction of CO is associated with the fact that it takes place only in the presence of water vapor, the products of whose decomposition (OH, H) are active centers. Since the quantity of OH and H is limited by the moisture content the reaction velocity cannot exceed a certain definite value. In section 1 we enumerated, in detail, the various properties of the flame propagation velocity in CO mixtures. Zeldovich analyzed the data of various foreign authors and also those of our coworker, Barsky, and showed that the properties of the CO flame and its absolute velocity may be obtained from our general theoretical formulas if it is assumed that the oxidizing reaction velocity of CO is determined by the following kinetic law:

$$\frac{d[\text{CO}_2]}{dt} = -2 \frac{d[\text{O}_2]}{dt} = - \frac{d[\text{CO}]}{dt} = Z e^{-\frac{25000}{RT}} [\text{H}_2\text{O}][\text{CO}] \quad (37)$$

We may note that H_2O appears only as a catalyzer and is not required in the course of the reaction. In order to present more clearly the reaction velocity according to (37) we construct a table of values of

$\omega = e^{-25000/RT}$ (the probability of the reaction computed for one impact of the molecules H_2O and CO) and the reaction times τ (time during which the products O_2 and CO are decreased to $1/e$ of their initial values).

TABLE 3

$T^\circ \text{ K}$	$\omega \times 10^3$	$\tau \text{ sec}$
1300	0.03	3×10^{-3}
1600	.33	3×10^{-4}
2000	2.8	3.5×10^{-5}
2400	7	1.4×10^{-5}
3000	25	4×10^{-6}

In order to compute the velocity of flame propagation according to the kinetic law of equation (37)

we shall distinguish case 1 when the initial gas contains CO in considerable excess of the stoichiometric quantity and case 2 when there is a deficiency of CO.

Case 1. - As we have already seen above, the reaction in the combustion zone occurs in a gas, the composition of which is near that of the final products. In the cooled final products the concentration of carbon monoxide will be $(CO)_1 = (CO)_0 - (CO_2)_1$ where $(CO)_0$ is the number of molecules of CO in a unit volume of the initial mixture and $(CO_2)_1$ is the number of molecules of CO_2 in a unit of volume of the final products (after their cooling to temperature T_0) or, what amounts to the same thing, the number of burned molecules of CO. In the combustion zone where the temperature is near the maximum temperature of combustion T_1 the number of CO molecules in unit volume (the actual concentration of CO) will be

$$[CO] = \frac{T_0}{T_1} [CO]_1$$

The number of molecules of H_2O in the combustion zone varies in relation to $(H_2O)_0$ only in the ratio T_0/T_1 since H_2O is not required in the reaction. Hence the actual concentration of H_2O will be

$$[H_2O] = \frac{T_0}{T_1} [H_2O]_0$$

Thus

$$w = Z e^{-E/RT} \left(\frac{T_0}{T_1} \right)^2 [H_2O]_0 [CO] \quad (38)$$

We see that in the above expression the oxygen concentration, that is, the only concentration which varies considerably in the combustion zone does not enter. Thus in relation to O_2 the reaction is of the first order and therefore the mathematical expression for the velocity of the flame propagation will be similar to formula (16).

For the sake of clearness, however, we shall derive

this expression from the general formula (12):

$$v_o = \frac{1}{\rho_o L} \sqrt{2\lambda Q' \int_{T_1}^{T_1} w \, dT} \approx \frac{1}{\rho_o L} \sqrt{2\lambda Q' \int_0^{T_1} w \, dT} \quad (39)$$

By substituting w from formula (38) and carrying out the corresponding computations, we find

$$v_o = \sqrt{1400 \frac{T_1 T_o^2}{E} e^{-E/RT} \frac{[H_2O]_o [CO]_1}{[CO_2]_1^2}} \quad (40)$$

where $E = 25,000$.

We shall derive formula (40). Substituting w from formula (38) under the integral sign of formula (39) we obtain

$$\int_0^{T_1} w \, dT = Z \frac{RT_1^2}{E} \left(\frac{T_o}{T_1}\right)^2 e^{-E/RT_1} [H_2O]_o [CO]_1 \quad (41)$$

$$v_o = \sqrt{2 \frac{\lambda Z}{\rho_o} \frac{Q'}{L \rho_o} \frac{1}{L} \frac{RT_1^2}{E} \left(\frac{T_o}{T_1}\right)^2 e^{-E/RT_1} [H_2O]_o [CO]_1} \quad (42)$$

According to the kinetic theory of gases the heat conductivity is

$$\lambda = \frac{1}{3} \rho_o C u$$

where C is the molecular specific heat of the mixture (at the combustion temperature $C \approx 9$)

$$Z = \sqrt{2\pi} \sigma^2 u = \frac{n}{n_1}$$

where n is the number of molecules in a unit volume of the mixture at the combustion temperature and equal to $n_0 T_0 / T_1$ (where n_0 is the number of molecules in the cold mixture). For $T = T_1$ the thermal velocity of the molecules is

$$u = u_{300} \sqrt{\frac{T_1}{300}}$$

where u_{300} is the velocity of the molecules at room temperature, that is, for our mixture $u_{300} \cong 5 \times 10^4$ cm/sec.

$$\frac{\lambda Z}{\rho_0} = \frac{1}{3} \frac{u^2 C}{\mu n_0} \frac{T_1}{T_0} \frac{\rho}{\rho_0} = \frac{1}{3} \frac{u^2 C}{\mu n_0} = \frac{75 \times 10^8}{300} \frac{T_1}{\mu n_0}$$

$$\frac{Q'}{L \rho_0} = \frac{1}{[CO_2]_1}$$

since $Q'(CO_2)_1 = L \rho_0$ is the heat given up in the combustion of a unit volume of the mixture.

$$L = \frac{M_0 Q}{\mu}$$

where M_0 is the ratio of the weight of the burning CO molecules to the weight of all molecules in the initial mixture, that is, in view of the nearness of the molecular weights of CO, O_2 and N_2 and because the burned CO is equal to $(CO_2)_1$

$$M_0 = \frac{[CO_2]_1}{n_0}$$

and hence

$$\frac{1}{L} = \frac{\mu n_0}{Q [CO_2]_1}$$

where the heat of formation of a molecule of CO_2 is $Q = 7 \times 10^4$ calories. Substituting all the obtained values in formula (42) we obtain formula (40) taking a mean value of $\mu \approx 30$.

Case 2. - For a deficiency of CO its concentration in the combustion zone is small and rapidly changes along the zone. Since the reaction velocity is proportional to (CO) we should here make use of the same derivation that was made above for monomolecular reactions. According to formula (21) the CO concentration in the combustion zone is

$$[\text{CO}] = [\text{CO}]_0 \frac{T_0}{T_1} \frac{\theta}{T_1 - T_0}$$

Substituting this expression in formula (37) and integrating we readily obtain

$$\int_{T_0}^{T_1} w \, dT \approx \frac{c_p}{L} \left(\frac{T_0}{T_1} \right)^2 \left(\frac{RT_1^2}{E} \right)^2 z e^{-E/RT_1} [\text{CO}]_0 [\text{H}_2\text{O}]_0 \quad (43)$$

Comparing this expression with (41) we see that the former differs only in that for the concentration $(\text{CO})_1$ there is substituted the magnitude $(\text{CO})_{\text{eff}} = \frac{c_p}{L} \frac{RT_1^2}{E} (\text{CO})_0$ and since for deficiency of CO $\frac{(\text{CO})_0}{L} = \frac{\rho_0}{Q'}$;

$$\text{CO}_{\text{eff}} = \frac{c_p \rho_0}{Q'} \frac{RT_1^2}{E} \quad (44)$$

For monomolecular reactions, however, as we have seen, this magnitude being multiplied by T_0/T_1 corresponds to the actual concentration (CO) in the reaction zone. Thus, the formula for the flame propagation velocity in mixtures with a deficiency of CO is the same as for the case of a considerable excess of CO except that instead of (CO) there is substituted $(\text{CO})_{\text{eff}}$. Practically, however, a considerable difference is obtained. Whereas in rich CO mixtures $(\text{CO})_1$ increases with increase in $(\text{CO})_0$, in rich O_2 mixtures $(\text{CO})_{\text{eff}}$ as is seen from formula (44)

does not depend on $(CO)_0$ if the combustion temperature is maintained constant (for example, with the aid of heating of the mixture by some method).

We thus arrive at the conclusion that the velocity of flame propagation in mixtures with equal combustion temperature remains constant for all mixtures with excess O_2 and is independent of the excess of O_2 . This conclusion was confirmed by our coworker, Barsky, who measured the velocity of flame propagation in mixtures with various excesses of oxygen and the same concentration $(CO)_0$ (varying the ratio O_2/N_2 in the mixture and thus maintaining a constant combustion temperature). The flame propagation velocity actually did not depend on the excess oxygen. On varying by the same method the CO content in mixtures with excess CO and keeping the quantity of oxygen the same (that is, again maintaining T_1 constant), Barsky, in correspondence with formula (40), showed that the velocity of flame propagation is proportional to the square root of the excess CO, that is, $\sqrt{(CO)_1}$.

For a simultaneous variation of both components the combustion temperature must necessarily likewise vary and it is impossible by such simple method to bring out the dependence of the reaction velocity on CO and O_2 . Experiments of this kind, conducted by other authors, are fundamentally in error. By utilizing, however, a certain initial preheating of the mixture it is possible to maintain T_1 constant on varying the ratio of the components. Making use of the data of Passauer and others (reference 5) Zel'dovich conducted such a test of the theory and arrived at the same result, namely, that the propagation velocity at constant T_1 does not depend on O_2 for an excess of O_2 and is proportional to $\sqrt{(CO)_1}$ for excess CO. According to formula (40) the propagation velocity is proportional to $\sqrt{(H_2O)_0}$ (that is, to the square root of the concentration or the partial pressure of the water vapor).

On replotting the results of Flock and Marvin, shown in figure 15, in coordinates $v - \sqrt{(H_2O)_0}$ we obtain good straight lines in agreement with the theory (figure 21). For large water vapor contents there are deviations for the reason at least that the thermal character of the mixture then begins to change.

As regards the dependence of the propagation velocity on the pressure of the mixture it follows from formula (40)

that for constant percent of moisture content the propagation velocity does not depend on the pressure (because $(\text{CO})_1$, $(\text{CO}_2)_0$, $(\text{H}_2\text{O})_0$ are proportional to p) and at constant partial vapor pressure v_0 is inversely proportional to \sqrt{p} . We know that just this kind of dependence on the pressure is observed in experiment.

It was most interesting to compare the computed absolute value of v_0 for mixtures of various ratios of CO to air. The computation led to the results shown by the dotted curve of figure 10. There are, to be sure, certain deviations from the test results in the region of the maximum but these, however, are of the same order of magnitude as the deviations in the test results. A similar computation for mixtures of CO with nitrogen and oxygen in various proportions likewise led to good agreement with the test results of Jahn given in figure 12. In general, it may be assumed said, that the approximate theory gives a fair description of the test results in this case.

A comparison was furthermore made between the computed and observed propagation velocities for various initial temperatures T_0 for various CO air mixtures. It was found that the deviations between theory and experiment in this case are not large. A qualitative explanation was also obtained of the fact that the increase of the propagation velocity with the pressure in oxygen mixtures is small. The fact is that whereas it is permissible with air mixtures not to take into account the incomplete combustion associated with dissociation, in the case of oxygen mixtures where temperatures up to 3000°K and above are developed, it is necessary to take dissociation into account. Details of the computation will be found in our article (reference 6) while here we give the result only. The computation leads to an increase of the velocity with the pressure as p^n where $n \approx 0.12$; whereas experiment gives the increase of the velocity with pressure as p^m where $m \approx 0.2$. Thus in this case (if the tests are considered reliable) the theory gives only the qualitatively correct result, namely, a small increase of v_0 with the pressure in rich oxygen mixtures.

Summarizing all that has been said above we may state that the new theory of combustion, through the choice of the form of kinetic law for the rate of oxidation of CO, which law contains only a single arbitrary constant ($E = 25,000$), rationally accounts for all the numerous experimental results on the flame propagation of CO in air and in oxygen,

quantitatively in most cases and qualitatively in only a few cases. It is very interesting to confirm directly the correctness of the kinetic law postulated by us for the rate of oxidation of CO. No experimental method, unfortunately, has up to the present time been developed for the study of the reaction kinetics at high temperatures such that the reaction proceeds halfway in a time interval of 10^{-3} - 10^{-4} seconds. We shall, therefore, proceed by a logical method and by examining closely the question of the mechanism of the oxidation of CO, attempt to find the required kinetic law.

It has been assumed that the catalytic action of water vapor in the oxidation of CO is based on a conversion reaction of the water vapor: $H_2O + CO = CO_2 + H_2$. The hydrogen thus obtained is soon oxidized and therefore the total oxidizing reaction proceeds with the reaction velocity of a conversion reaction. Assuming that the conversion proceeds according to the simple bimolecular law we very simply arrive at the required law for the oxidation of CO:

$$w = Ze^{-E/RT}[CO][H_2O]$$

Assuming the activation energy of the conversion reaction equal to 25,000 calories we obtain the law (37) employed by us. Unfortunately the velocity of conversion computed by the above formula does not at all correspond to the meager experimental facts which are available for the study of a homogeneous conversion reaction. Such a reaction in technical procedure, as is known, occurs with catalyzers and therefore few have concerned themselves with homogeneous conversion. On the velocity of conversion there are available data by Thompson (reference 7) and Kondratyev (reference 8) for reactions in quartz vessels at $T \approx 1000^\circ K$. For the conversion velocity under these conditions Thompson obtains $e^{-E/RT} = 2.5 \times 10^{-14}$ and Kondratyev a value one hundred times as large, namely, 10^{-12} . According to formula (37) the value obtained is approximately 10^{-6} , that is, 10^8 times as large compared with the results of Thompson and 10^6 times as large compared with the results of Kondratyev. The results of Thompson should be considered as more correct because he experimented with a vessel of greater radius and the possibility of catalysis by the wall was less probable than was the case with Kondratyev. In any case

we see there can be no question of such a simple explanation of the law (37).

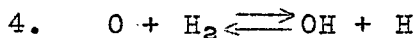
Investigations of the velocity of the oxidation reaction of CO at temperatures of the order of 1000°K in the presence of water vapor show that this reaction is complicated by the chain process, the velocity being proportional to $(\text{CO})(\text{H}_2\text{O})$ and inversely proportional to (O_2) . It is very probable, however, that under these conditions the primary active centers required for the start of the chain arise at the walls of the vessel as a result of a heterogeneous process, which, of course, does not occur at high temperatures and especially in flames. For this reason the extrapolation of the data obtained under the above-mentioned conditions to the flame will hardly be justified. Moreover, reactions in closed vessels have received but little study. We are fully justified in stating, however, that a reaction which appears as a chain reaction at $T \approx 1000^{\circ}$ remains a chain reaction at any high temperature whatever. It is well known, moreover, that the flames of moist CO reveal in the spectrum the OH radical. Kondratyev furthermore, quantitatively measured (by the method of light absorption) the concentration of the OH radicals in rarified flames in moist CO having a temperature of $1000^{\circ} - 1200^{\circ}\text{K}$ and showed that the concentration of OH exceeds its equilibrium value a thousand times. These facts clearly indicate that the OH radical is one of the active centers of the chain oxidizing reaction of CO.

Analyzing all possible chain mechanisms of this type, we arrived at the conclusion that only one of them is logically possible at high temperatures. This chain consists of the following steps of elementary reactions:

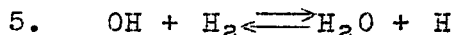
- | | | |
|----|--|-----------------|
| 1. | $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ | } Chain |
| 2. | $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ | |
| 3. | $\text{O} + \text{CO} = \text{CO}_2$ | |
| 4. | $\text{O} + \text{H}_2 = \text{OH} + \text{H}$ | Branched chains |
| 5. | $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$ | |

As a result of the branching of the chain the total oxidizing reaction will be accelerated in time until the

concentrations of OH and H reach values such that the reverse reaction of (4) $\text{OH} + \text{H} \rightleftharpoons \text{H}_2 + \text{O}$ balances the direct reaction $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$. After this a stationary oxidizing reaction is established. It is easy to show that the direct reactions 4 and 5 will be in equilibrium with the reverse reactions, that is, in the reaction zone there will occur the equilibriums



and



The equilibrium constants K_4 and K_5 of these reactions are well known.

As regards the constants K_1 , K_2 , and K_3 corresponding to the velocities of reaction 1, 2, and 3 the situation is less favorable. For the constants K_1 and K_2 there are approximately known the activation energies $E_1 = 26,000 \pm 4000$, $E_2 = 10,000 \pm 3000$. The coefficient before the exponential for the first reaction is not known and for the second is of the order 0.01Z. No study was made at all of the constant K_3 . If it is assumed that reaction 3 occurs for every third impact then at atmospheric pressure $K_3 \approx 10^{-3}$. If the most probable values of the constants from the experimental and theoretical points of view are taken, the series of reactions leads to a kinetic law which agrees with expression (37) in the sense of the dependence of the velocity on the temperature and on the concentrations (CO) and (H_2O); (it gives a practical non-dependence on (O_2)). For mixtures with excess CO, however, it gives an absolute reaction velocity about 10 times less than the actual. Since the measured values of the kinetic constants of the elementary reactions are bad the matter is evidently associated with the not entirely correct choice of these constants. In general, we may say, that the check of the new theory on the oxidation of CO leads to satisfactory results.

Translation by S. Reiss,
National Advisory Committee
for Aeronautics.

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NACA Technical Memorandum No. 1026

Continuation of Figures 11, 12, 15

Key for Figure 11

1 - 87% N ₂ +13% O ₂ ;	2 - 83% N ₂ + 17% O ₂ ;
3 - 79% N ₂ +21% O ₂ ;	4 - 70% N ₂ + 30% O ₂ ;
5 - 60% N ₂ +40% O ₂ ;	6 - 40% N ₂ + 60% O ₂ ;
7 - 20% N ₂ +80% O ₂ ;	8 - 1.5% N ₂ +98.5% O ₂ ;

Key for Figure 12

1 - 87.5% N ₂ +12.5% O ₂ ;	2 - 85% N ₂ +15% O ₂ ;
3 - 82.5% N ₂ +17.5% O ₂ ;	4 - 79% N ₂ +21% O ₂ ;
5 - 75% N ₂ +25% O ₂ ;	6 - 70% N ₂ +30% O ₂ ;
7 - 65% N ₂ +35% O ₂ ;	8 - 60% N ₂ +40% O ₂ ;
9 - 50% N ₂ +50% O ₂ ;	10 - 40% N ₂ +60% O ₂ ;
11 - 30% N ₂ +70% O ₂ ;	12 - 20% N ₂ +80% O ₂ ;
13 - 10% N ₂ +90% O ₂ ;	14 - 1.5% N ₂ +98.5% O ₂ ;

Key for Figure 15

1 - PCO+O ₂ = 100 mm;
2 - PCO+O ₂ = 150 mm;
3 - PCO+O ₂ = 200 mm;
4 - PCO+O ₂ = 300 mm;
5 - PCO+O ₂ = 760 mm;

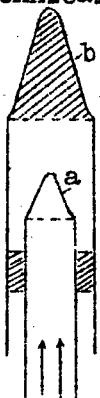


Figure 1.

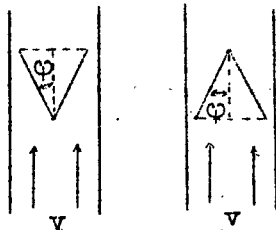


Figure 7.

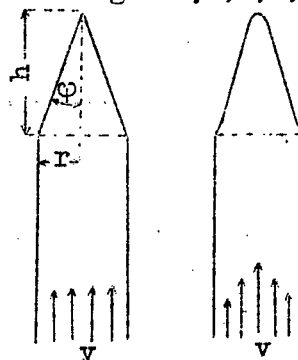


Figure 8.

Figure 9.

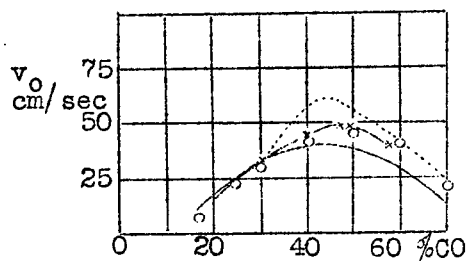


Figure 10.- Normal velocity of flame propagation of carbon monoxide-air mixtures.

Full curve - tests of Passauer,
 x - tests of Chitrin,
 o - tests of Barsky,
 □ - tests of Jahn. The dotted curve was computed by the formulas of the new theory of the flame propagation with the kinetic law (37).

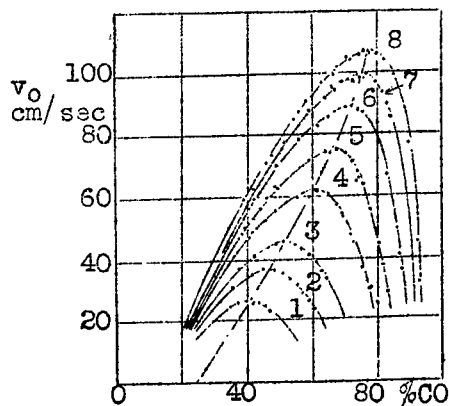


Figure 11.- Normal velocity of flame propagation in mixtures of CO with atmospheric $N_2 + O_2$. The percent composition of $N_2 + O_2$ of each curve is constant (Jahn).

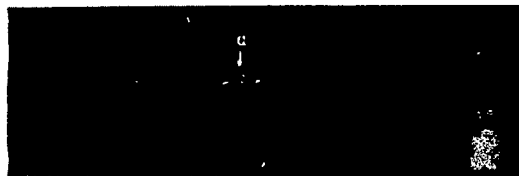


Figure 3.- Wave front moving in a horizontal tube ($d = 5$ cm). The burning mixture consists of 55 percent CO and 45 percent air. At point a flame oscillations arise. (photograph by Barsky).

Figure 2



Figure 4.- An example of uniform flame propagation. (Photograph taken on a rotating film by Sokolik).



Figure 5



Figure 6

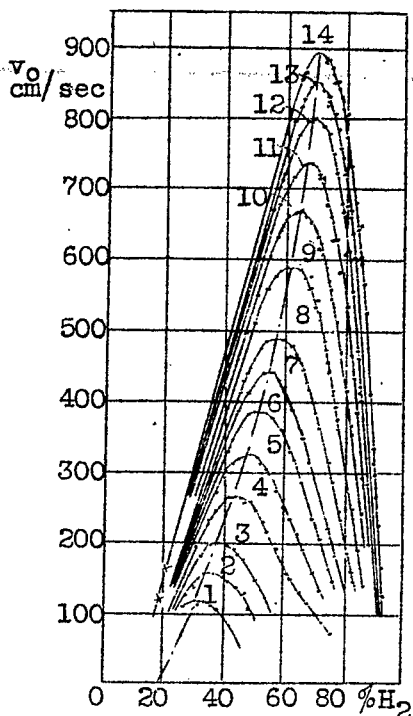


Figure 12.- Normal velocity of flame propagation in mixtures of hydrogen with atmospheric $N_2 + O_2$. The percent of $N_2 + O_2$ along each curve is constant (Jahn).

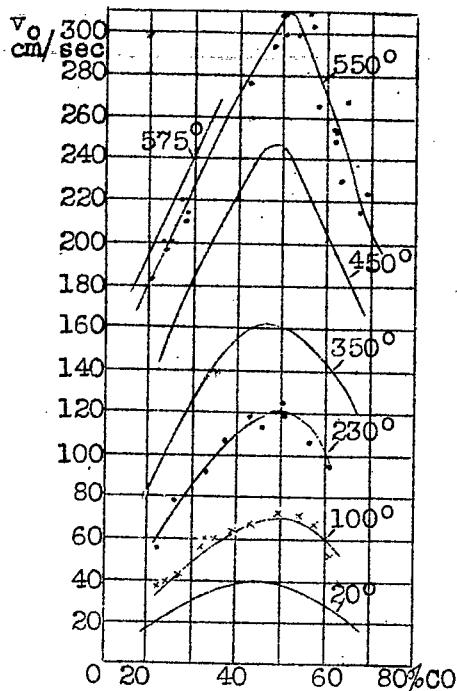


Figure 14.

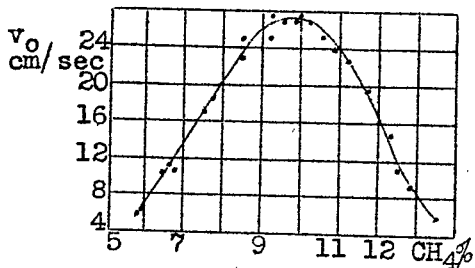


Figure 13.- Normal velocity of flame propagation in methane-air mixtures (Coward and Hartwell).

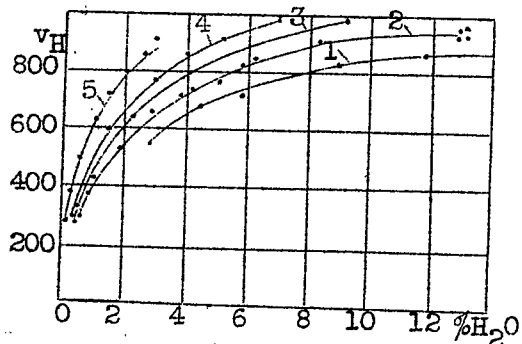


Figure 15.

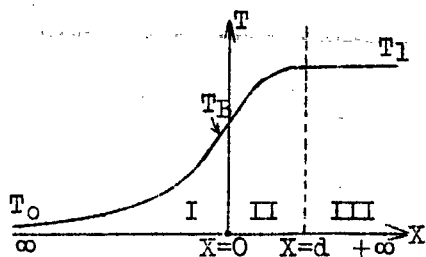


Figure 16

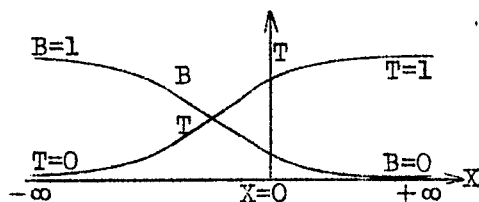


Figure 17

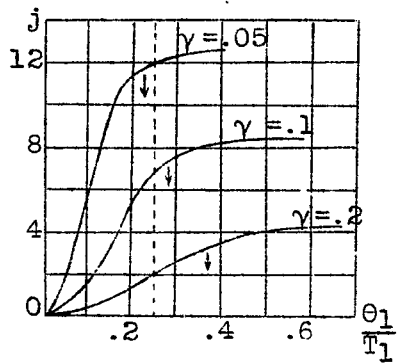


Figure 18

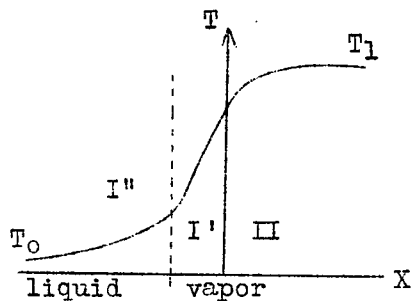


Figure 19

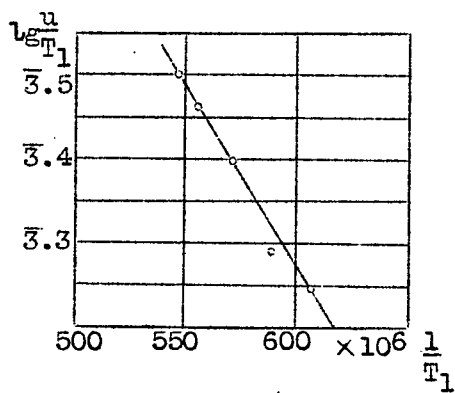


Figure 20

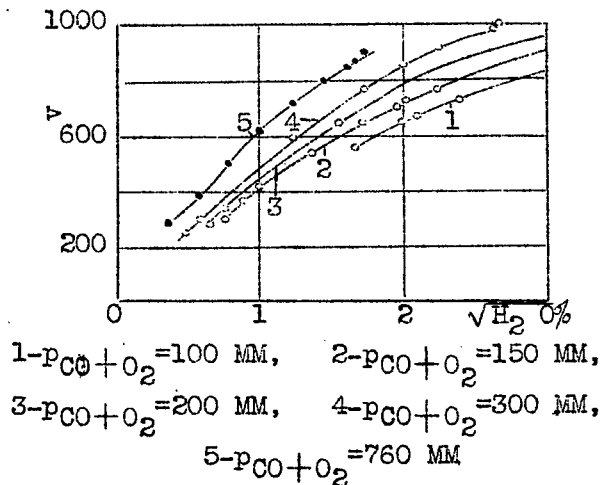


Figure 21

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